

TECHNOLOGY OF CELLULOSE ESTERS

A THEORETICAL AND PRACTICAL TREATISE ON THE ORIGIN,
HISTORY, CHEMISTRY, MANUFACTURE, TECHNICAL APPLICATION,
AND ANALYSIS OF THE PRODUCTS OF ACYLATION AND
ALKYLATION OF NORMAL AND MODIFIED CELLULOSE, INCLUDING
NITROCELLULOSE, CELLULOSE, PYROXYLIN, COLLODION,
CELLOIDIN, GUNCOTTON, ACETYLCELLULOSE AND X-CELLULOSE,
AS APPLIED TO TECHNOLOGY, PHARMACY, MICROSCOPY,
MEDICINE, PHOTOGRAPHY, AND THE WARLIKE
AND PEACEFUL ARTS.

IN TEN VOLUMES

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This Table of Contents contains an enumeration of the 637 main topics only, the five hundred forty sub-topics not being indicated herein.

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ABBREVIATIONS.

| | | | |
|-------------|---|----------|---|
| A. A. A. S. | American Association for the Advancement of Science | h. p. | horse power |
| Anon. | Anonyme (Anonymous) | hr. | hour(s) |
| A. O. A. C. | Association of Official Agricultural Chem- ists | insol. | insoluble |
| abs. | absolute | in. | inch |
| A. C. | Alternating current | k. | kilogram |
| Act. | Action | kw. | kilowatt |
| Add. | Addition Patent | l. | liter(s) |
| alc. | alcohol ethyl | /. | laevo |
| alk. | alkaline | lab. | laboratory |
| amp. | ampere | lb. | Avoirdupois pound(s) |
| amt. | amount | Ltd. | Limited |
| approx. | approximate | m. | meter |
| at. | atom, atomic | m. | meta |
| atm. | atmosphere(s) | mfr. | manufacturer |
| atm. pr. | atmospheric pressure | mfg. | manufacturing |
| as- | asymmetric | mgm. | milligram |
| av. | average | min. | minute(s) |
| b. | boil(s), boiling | mm. | millimeter |
| b. pt. | boiling point | mol. | molecule(s) |
| c. | asymmetric carbon atom | mol. wt. | molecular weight |
| cal. | calorie | m. pt. | melting point |
| cc. | cubic centimeter(s) | M. S. | Mild steel |
| chem. | chemical | nor. | normal |
| C. I. | cast iron | n. t. p. | normal temperature and pressure (0° C, 760 mm.) |
| com. | commercial | o- | ortho |
| comp. | composition | ord. | ordinary |
| compd. | compound | oz. | Avoirdupois ounce |
| conc. | concentrat-ed, ion | p- | para |
| cor. | corrected | pp. | precipitate |
| C. O. V. | Concentrated oil of vit- riol | p. | pint |
| c. p. | candle power | qt. | quart |
| crys. | crystals, crystallized | quant. | quantitative |
| cu. | cubic | recryst. | recrystallized |
| cu. ft. | cubic foot (feet) | r. p. m. | revolution per minute |
| cu. m. | cubic meter(s) | sat. | saturate(d) |
| cwt. | hundredweight | sc. | scruple |
| D. C. | Direct current | sec. | second(s) |
| d- | dextro | soln. | solution |
| d. | density | Soc. | Societe |
| diam. | diameter | sp. gr. | specific gravity |
| dm. | decimeter | sq. | square |
| dil. | dilute | S. T. P. | Standard temperature (15.56° C.) and pres- sure (760 mm.) |
| dr. | dram | sym. | symmetrical |
| fl. | fluid | temp. | temperature(s) |
| Farb. | Farbenfabriken | v- | vicinal |
| f. pt. | freezing point | vac. | vacuum |
| gal. | U. S. gallon, 3785 cc. | vol. | volume(s) |
| Ges. | Gesellschaft | wt. | weight |
| gm. | gram(s) | ° | degrees Centigrade (al- ways) |
| gr. | grain(s) | % | per cent. by weight |

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| Chapt. | Pages | Topics | Tables | Cuts | Foot Notes | Patents | Literature Refer- ences | Names |
|--------|-------|--------|--------|------|---------------|---------|-------------------------------|-------|
| I | 388 | 75 | 32 | 0 | 1124 | 3624 | 13665 | 5042 |
| II | 96 | 19 | 2 | 0 | 798 | 896 | 6583 | 1830 |
| III | 98 | 27 | 19 | 1 | 174 | 143 | 565 | 211 |
| IV | 82 | 11 | 0 | 40 | 111 | 238 | 508 | 466 |
| V | 344 | 71 | 1 | 41 | 1199 | 5116 | 10386 | 4994 |
| VI | 396 | 141 | 13 | 25 | 1676 | 4009 | 9376 | 5011 |
| VII | 116 | 21 | 2 | 30 | 100 | 111 | 509 | 155 |
| VIII | 48 | 0 | 34 | 0 | 12 | — | 7 | 20 |
| IX | 366 | 65 | 33 | 3 | 1420 | 1175 | 8359 | 1988 |
| X | 340 | 54 | 11 | 138 | 320 | 577 | 1014 | 351 |
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| XII | 707 | 88 | 0 | 2 | 12473 | 22963 | 28316 | 12461 |
| Total | 3085 | 599 | 150 | 294 | 19611 | 39458 | 80504 | 33740 |

LIST OF ABBREVIATIONS TO LITERATURE

Prepared by DR. CARL MARX

| | |
|-----------------------------------|---|
| A. and N. J. | Army and Naval Journal |
| •Aarau, Archiv der Med. | Archiv. der Medizin, Chirurgie, und Pharmazie |
| Aarau, Mitth. | Mittheilungen des Aargauischen Naturforschenden Gesellschaft |
| Abbeville, Bull. Soc. Linn. | Compte Rendu et Bulletin de la Société Linnéenne du Nord de la France |
| Abbeville, Mem. Soc. Emul. | Memoires de la Société d'Emulation d'Abbeville |
| Abeille, J. | L'Abeille, Journal d'Entomologie |
| Abeille mem. | L'Abeille: memoires d'Entomologie |
| Abeille Soc. | (Publications de la Soc. Entomologie de France.) La Abeille. Journal de Entomologie |
| Acad. | Memoires de l'Academie des Sciences |
| Acad. Caes. Leop. Nova Acta | Nova Acta physico-medica Academiae Caes. Leopoldino-Carolinae Naturae Curiosorum |
| Acad. Natur. Curios. Nova Acta | Nova Acta Academiae Caesariae Leopoldino-Carolinae Germanicae Naturae Curiosorum |
| Acireale Accad. Atti | Atti e Rendiconti dell' Accademia di Scienze, Lettere e Arti dei Zelanti e PP. dello Studio di Acireale |
| Acireale, Soc. Ital. Micro. Boll. | Bollettino della Societa Italiana dei Microscopisti |
| Acquoy, Tijdschrift | Tijdschrift voor Wis-, Natuur-, en Wertuigkunde |
| Acta Math. | Acta Mathematica |
| Actes Soc. Helvetique | Actes de la Société Helvétique des Sciences Naturelles |
| Adansonia | Adansonis: Recueil d'observations botaniques |
| Adelaide Phil. Soc. Trans. | Transactions and Proceedings and Report of the Philosophical Society of Adelaide, South Australia |
| Aeronaut. J. | The Aeronautical Journal |
| Aeronaut. Soc. Reports | Annual Reports of the Aeronautical Society of Great Britain |
| Aeronaute | L'Aeronaute: bulletin mensuel international de la Navigation Aérienne |
| Afhandl. Fysik. | Afhandlingar i Fysik, Kemi, och Mineralogi |
| African Assoc. Proc. | Proceedings of the African Association for promoting the Discovery of the Interior Parts of Africa |
| Agen, Soc. Agric. Recueil. | Recueil des Travaux de la Société d'Agriculture, Sciences, et Arts d'Agen |
| Agram., Program Gymnas. | Program des k. k. Akademischen Gymnasiums zu Agram |
| Agric. Gaz. | The Agricultural Gazette |
| Agric. Gaz. N. S. Wales | Agricultural Gazette of New South Wales, The |
| Agric. J. India | Agricultural Journal of India |
| Agric. Ledg. | Agricultural Ledger |
| •Agric. Soc. J. | The Journal of the Royal Agricultural Society of England |
| Agric. Stud. Gaz. | Agricultural Students' Gazette. A Quarterly Journal edited by Students at the College, Cirencester |
| ••Agron. Ztg. | Agronomische Zeitung |
| Aix, Acad. Mem. | Recueil de Memoires de la Société des Amis des Sciences, des Lettres, de l'Agriculture, et des Arts a Aix |

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|---------------------------------------|--|
| Albany Inst. Proc. | Proceedings of the Albany Institute |
| Albany Inst. Trans. | Transactions of the Albany Institute |
| Alger. Bull. Soc. Climat. | Bulletin de la Société de Climatologie Algerienne |
| Alk. | Alcohol |
| Allelod. Soc. Trans. | The transaction of the Allelopathic Society |
| Allg. Berg. Ztg. | Allgemeine berg- und hüttenmännische Zeitung |
| Allg. Bot. Zts. | Allgemeine Botanische Zeitschrift für Systematik, Floristik, Pflanzengeographie, etc. |
| Allg. Deut. Naturhist. Ztg. | Allgemeine Deutsche naturhistorische Zeitung |
| Allg. Deut. Ornith. Ges. | See J. Ornith |
| Allg. Fischerei Ztg. | Allgemeine Fischerei Zeitung |
| Allg. Forst-Jagd-Zts. | Allgemeine Forst- und Jagd-Zeitung |
| Allg. Gerber-Ztg. | Allgemeine Gerber-Zeitung |
| Allg. Schweiz. Ges. Gesam. Naturwiss. | See Zürich, Schweiz. Ges. N. Denkschr. |
| Allg. Syn. Suikerfab. | Algemeen Syndicat van Suikerfabrikanten in Nederl. Indie. With Arch-Suikerind, etc. |
| Allg. Zts. Bierbr. Malzfabr. | Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation |
| Allier, Bull. Soc. Emul. | Bulletin de la Société d'Émulation du département de l'Allier: Sciences, Arts, et Belles-Lettres |
| Alpina | Alpina, eine Schrift der genauen Kenntniss der Alpen gewidmet; von Carl Ulisses von Salis und J. R. Steinnueller |
| Altenburg Mitth. | Mittheilungen aus dem Osterlande; herausgegeben von der Naturforschenden Gesellschaft zu Altenburg |
| Amat. Mechan. Soc. J. | The (Quarterly) Journal of the Amateur Mechanical Society |
| Amer. Acad. Mem. | Memoirs of the American Academy of Arts and Sciences |
| Amer. Acad. Proc. | Proceedings of the American Academy of Arts and Sciences |
| Amer. Agric. | American Agriculturist |
| Amer. Ann. Phot. | American Annual of Photography |
| Amer. Apoth. Ztg. | Deutsch-Amerikanische Apotheker Zeitung |
| Amer. Artisan | American Artisan |
| Amer. Assoc. Proc. | Proceedings of the American Association for the Advancement of Science |
| Amer. Brewers Rev. | American Brewers Review |
| Amer. Builder | The American Builder |
| Amer. Chem. J. | American Chemical Journal |
| Amer. Chemist | American Chemist |
| Amer. Drug. | American Druggist and Pharmaceutical Record |
| Amer. Electrochem. Soc. | American Electrochemical Society |
| Amer. Engin. & Railroad J. | American Engineer (Car Builder), and Railroad Journal |
| Amer. Ethnol. Soc. Trans. | Transactions of the American Ethnological Society |
| Amer. Entom. Soc. Trans. | Transactions of the American Entomological Society and Proceedings of the Entomological Section of the Academy of Natural Sciences |
| Amer. Fertilizer | American Fertilizer, The |
| Amer. Food J. | American Food Journal |
| Amer. Gas Light J. | American Gas Light Journal, The |
| Amer. Geogr. Soc. Bull. | Bulletin of the American Geographical and Statistical Society |
| Amer. Geogr. Soc. J. | Journal American Geographical Society, New York |
| Amer. Geogr. Soc. Proc. | Proceedings of the American Geographical and Statistical Society of New York |

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| Amer. Geol. and Nat. As- soc. Reports | Reports of the Meetings of the Association of Ameri- can Geologists and Naturalists at Philadelphia |
| Amer. J. Conchol. | American Journal of Conchology |
| Amer. J. Dent. Sci. | American Journal of Dental Science |
| Amer. J. Math. | American Journal of Mathematics |
| Amer. J. Med. Sci. | American Journal of the Medical Sciences. |
| Amer. J. Otol. | The American Journal of Otology |
| Amer. J. Pharm. | American Journal of Pharmacy |
| Amer. J. Physiol. | The American Journal of Physiology |
| Amer. J. Physiol., Boston | American Journal of Physiology, Boston |
| Amer. J. Psychol. | The American Journal of Psychology |
| Amer. J. Pub. Health | American Journal of Public Health |
| Amer. J. Sci. | The American Journal of Science |
| Amer. Mach. | American Machinist |
| Amherst. Math. Soc. | See N. Y. Amer. Math. Soc. |
| Amer. Med. | American Medicine |
| Amer. Med. Assoc. Trans. | Transactions of the American Medical Association |
| Amer. Med. Phil. Reg. | The American Medical and Philosophical Register; or Annals of Medicine, Natural History, Agriculture, and the Arts |
| Amer. Med. Recorder | American Medical Recorder |
| Amer. Meteorol. J. | American Meteorological Journal |
| Amer. Micro. J. | The American Quarterly Microscopical Journal. With which is also published the Transaction of the New York Microscopical Society |
| Amer. Micro. Soc. Proc. | Proceedings of the American Microscopical Society |
| Amer. Micro. Soc. Trans. | Transactions of the American Microscopical Society |
| Amer. Mineral. J. | The American Mineralogical Journal |
| Amer. Min. Gaz. | The American Mining Gazette and Geological Maga- zine |
| Amer. Monthly Micro. J. | American Monthly Microscopical Journal |
| Amer. Mus. Bull. | Bulletin of the American Museum of Natural History |
| Amer. Mus. Mem. | Memoirs of the American Museum of Natural History |
| Amer. Natur. | American Naturalist |
| Amer. Ophthalm. Soc. Trans. | Transactions of the American Ophthalmological So- ciety |
| American Perfumer | American Perfumer and Essential Oil Review, The |
| Amer. Phil. Soc. Proc. | Proceedings of the American Philosophical Society held at Philadelphia |
| Amer. Phil. Soc. Trans. | Transactions of the American Philosophical Society, held at Philadelphia, for promoting useful knowledge |
| Amer. Phot. | American Photography |
| Amer. Poly. J. | The American Polytechnic Journal |
| Amer. Quart. J. Agric. | American Quarterly Journal of Agriculture and Science |
| Amer. Reports State Entom. | See Ill., Mass., Mo., N. Y. |
| Amer. Soc. Agr. Sci. Proc. | Proceedings of the Society for the Promotion of Agri- cultural Science |
| Amer. Soc. Civ. Engin. Trans. | Transactions of the American Society of Civil Engineers |
| Amer. Soc. Micro. Proc. | Proceedings of the American Society of Microscopists |
| Amer. Sugar. Ind. | American Sugar Industry and Beet Sugar Gazette, The |
| Amer. Vet. Rev., N. Y. | American Veterinary Review, N. Y. |
| Amherst. Agric. Sta. Re- port | Annual Report of the State Agricultural Experiment Stations, at Amherst, Mass. |
| Amici, Giorn. Loscano | Giornale Loscano di Scienze mediche, fisiche e naturali |
| Amiens Acad. Sci. Mem. | Memoirs de l'Academie des Sciences, des Lettres et des Arts d'Amiens |

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|---|---|
| Ammon, Monatschr. Med. | Monatschrift für Medecin, Augenheilkunde, und Chirurgie |
| Ammon, Zts. Ophthalm. | Zeitschrift für die Ophthalmologie |
| Amsterdam | Werken van het Genootschap ter Bevordering der Natuur-, Geneesen Heelkunde. See Maandbl. Nat. |
| Amsterdam, Akad. Jaarb. | Jaarboek van de koninklijke Akademie van Wetenschappen gevestigd te Amsterdam |
| Amsterdam, Akad. Proc. | Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences |
| Amsterdam, Akad. Verh. | Verhandelingen der koninklijke Akademie van Wetenschapp. |
| Amsterdam, Akad. Versl. Mededeel. | Verslagen en Mededeelingen der Koninklijke Akademie van Wetenschappen. Afdeling Naturkunde |
| Amsterdam, ° Akad. Wet. Proc. | Processen-Verbaal van de gewone Vergaderingen der Koninklijke Akademie van Wetenschappen. ° Afdeling Naturkunde. |
| Amsterdam, Archief Wisk. Genoots. | Archief uitgegeven door het Wiskundig Genootschap |
| Amsterdam Bijdr. Dierk. | Bijdragen tot de Dierkunde uitgegeven door the (Koninklijk Zoologisch) Genootschap Natura Artis Magistra, te Amsterdam |
| Amsterdam, Bull. Congr. Bot. | Bulletin du Congres International de Botanique et d'Horticulture reuni a Amsterdam |
| Amsterdam Congr. Bot. Actes | Actes du Congres International de Botanistes, d'Horticulteurs. tenu a Amsterdam, en 1877 |
| Amsterdam Genootsch. "Natura Artis Magistra" | See Amsterdam Bijdr. Dierk |
| Amsterdam Genootsch. Nat., Genees- en Heelkunde | See Maandbl. Nat. |
| Amsterdam, Het Inst. | Het Instituut |
| Amsterdam, Mengelwerk | Mengelwerk van uitgelezen en andere Wisen Natuurkundige Verhandelingen |
| Amsterdam, Nieuw. Verh. | Nieuwe Verhandelingen der eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, en Schoone Kunsten te Amsterdam |
| Amsterdam, Nieuw. Wis. Voorstel. | Verzameling van nieuwe wiskundige Voorstellen door de Leden van het Wiskundig Genootschap, onder de zinspreuk: <i>Een onvermoeide arbeid komt alles te boven</i> , elkander tot onderlinge oefening opgegeven |
| Amsterdam Nederl. Aardr. Genootsch. Tijdschr. | Tijdschrift van het (Kon.) Nederlandsch. Aardrijkskundig Genootschap, gevestigd te Amsterdam |
| Amsterdam, Onderz. Phys. Lab. | Onderzoekingen gedaan in het Physiologisch Laboratorium van de Doorluchtige en Klinische Scholen te Amsterdam |
| Amsterdam, Tijdschr. Natuurk. Wetens. | Tijdschrift voor Natuurkundige Wetenschappen en Kunsten |
| Amsterdam, Tijdschr. Wis. Natuurk. Wetens. | Tijdschrift voor de Wis- en Natuurkundige Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam |
| Amsterdam, Verh. | Verhandelingen der Eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam |
| Amsterdam, Verh. Genoots. Geneesk. | Verhandelingen van het Genootschap ter Bevordering der Geneesen Heilkunde, en Schoone Kunsten te Amsterdam |
| Amsterdam, Verzam. Ber. Navig. | Verzameling van Berichten over eenige onderwerpen des Navigatie |

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| Amsterdam Zool. Genootsch. "Natura Artis Magistra" | See Nederl. Tijdschr. Dierk. |
| Anales agron. | Anales Agronomicos |
| Anales fis. quim. | Anales de la sociedad española de fisica y química |
| Anales inst. med. nacional | Anales del instituto medico nacional |
| Anales Minería Mex. | Anales de la Minería Mexicana, Revista de Minas |
| Analyst | The Analyst, including the Proceedings of the Society of Public Analysts |
| Anat. | Anatomie |
| Anat. Anz. | Anatomischer Anzeiger. Centralblatt für die Gesamte Wissenschaftliche Anatomie. (Amtliches Organ der Anatomischen Gesellschaft) |
| Anat. Ges. | See Anat. Anz. |
| Anat. Hefte | Anatomische Hefte. Referate und Beiträge (Beiträge und Referate) zur Anatomie und Entwicklungsgeschichte. |
| Anat. Soc. Proc. | See J. Anat. Physiol. |
| Anat. Studien | Anatomische Studien |
| Angers Acad. Sci. Mem. | Memoires de l'Academie des Sciences et Belles-Lettres d'Angers |
| Angers, Ann. Soc. Linn | Annales de la Société Linneenne du département de Maine et Loire |
| Angers, Mem. Soc. Agric. | Mémoires de la Société d'Agriculture, Sciences, et Arts |
| Angers, Soc. Sci. Bull. | Bulletin de la Société d'Etude des Scientifiques d'Angers |
| Ann. | Liebig's Annalen der Chemie |
| Ann. Bot. | Annals of Botany |
| Ann. Chim. | Annales de Chimie |
| Ann. Chim. anal. | Annales de Chimie analytique applique à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie |
| Ann. chim. farm. | Annali di Chimica e de farmacologia |
| Ann. Chim. Phys. | Annales de Chimie et de Physique |
| Ann. Chimica | Annali di Chimica (Medico-Farmaceutica e di Farmacologia) |
| Ann. Conduct. Ponts et Chauss. | Annales des Conducteurs des Ponts et Chaussées et des Gardes-Mines |
| Ann. Conserv. Arts Met. | Annales du Conservatoire des Arts et Metiers |
| Ann. Dermatol. | Annales de Dermatologie et de Syphiligraphie |
| Ann. Ecole norm. | Annales scientifiques de l'Ecole Normale superieure (I. Pasteur) |
| Ann. Falsif. | Annales des Falsifications |
| Ann. Farm. Chim. | Annali di Farmacoterapia e Chimica (Biologica) |
| Ann. Fis. Chim. | Annali di Fisica, Chimica, etc. |
| Ann. Génie Civil | Annales du Génie Civil |
| Ann. Gén. Sci. Phys. | Annales générales des Sciences Physiques |
| Ann. Geogr. | Annales de Géographie |
| Ann. Hydrogr. | Annales Hydrographiques |
| Ann. Hydrogr. Mar. Met. | Annalen der Hydrographie und Maritimen Meteorologie. Organ des Hydrographischen Bureaus (Amtes) und der Deutschen Seewarte |
| Ann. hyg. pub. | Annales d'hygiène publique |
| Ann. Ind. | Annales industrielles, par Fredureau, etc. |
| Ann. Inst. Pastuer | Annales de l'Institut Pasteur |
| Ann. Landw. | Annalen der Landwirthschaft in den K. Staaten |
| Ann. Landw. Wochenbl. | Annalen der Landwirtschaft, Wochenblatt |
| Ann. Mag. Natur. Hist. | The Annals and Magazine of Natural History, including Zoology, Botany, and Geology |

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| Ann. Matemat. | Annali di Matematica pura ed applicata |
| Ann. Mat'a. | Annals of Mathematics |
| Ann. Med. | Annali di Medicina |
| Ann. Med. Psychol. | Annales medico-psychologiques; Journal de l'anatomie, Physiologie, etc., du système nerveux |
| Ann. Med. Surg. | Annals of Medicine and Surgery, or Records of the occurring Improvements and Discoveries in Medicine, Surgery, and their immediately connected Arts and Sciences |
| Ann. Microgr. | Annales de Micrographie spécialement consacrées a la Bacteriologie, aux Protophytes et aux Protozoaires |
| Ann. Mines | Annales des Mines . . . redigees et publiees sous l'Autorisation du Ministre des Travaux Publics |
| Ann. Musco Ind. Itál. | Annali del R. Museo Industriale Italiano |
| Ann. Natur. Hist. | Annals of Natural History |
| Ann. Oculist | Annales d'Oculistique et de Gynecologie |
| Ann. Pharm. | Annals of Pharmacy |
| Ann. Pharm. Louvain | Annales de Pharmacie, Louvain |
| Ann. Phil. | Annals of Philosophy |
| Ann. Phys. | Annalen der Physik |
| Ann. Phys. Chem. | Annalen der Physik und Chemie |
| Ann. Ponts et Chauss. | Annales des Ponts et Chaussées |
| Ann. R. Staz. Chim. | Annali della R. Stazione Chimico Agraria Sperimentale di Roma |
| Ann. Rep., U. S. Dept. Agric. | Annual Report of the United States Department of Agriculture |
| Ann. sci. agron. | Annales de la science agronomique française et étrangère |
| Ann. Sci. Bot. Nat. | Annales des Sciences Naturelles, Botanique |
| Ann. Sci. Lomb. Veneto | Annali delle Scienze del Regno Lombardo-Veneto |
| Ann. Sci. Nat. | Annales des Sciences Naturelles. Botanique. Zoologie et Patontologie, comprenant l'Anatomie, la Physiologie, la Classification et l'Histoire Naturelle des Animaux |
| Ann. Sci. Univ. Jassy | Annales scientifiques de l'Université de Jassy |
| Ann. Scott. Natur. Hist. | The Annals of Scottish Natural History |
| Ann. Surg. | Annals of Surgery |
| Ann. Storia Natur. | Annali di Storia Naturale |
| Ann. Telegr. | Annales Telegraphiques |
| Annab.-Buchh. Ver. Naturk. Ber. | Bericht über den Annaberg-Buchholzer Verein für Naturkunde |
| Annab.-Buchh. Ver. Naturk. Jahr. | Jahresbericht des Annaberg-Buchholzer Vereins für Naturkunde |
| Annaes Sci. Natur. | Annaes de Sciencias Naturaes |
| Année Biol. | L'Année Biologique. Comptes Rendus annuels des Travaux de Biologie Generale |
| Annot. Zool. Jap. | Annotationes Zoologicae Japonenses, Auspiciis Societatis Zoologicae Tokyonensis seriatim editae |
| Annuaire Ancienne Normandie | Annuaire des cinq. Departements de l'Ancienne Normandie, par l'Association Normandie |
| Annuaire Inst. Provinces | Annuaire de l'Institut des Provinces, des Societés Savantes, et des Congres Scientifiques |
| Annuaire met. France | Annuaire Meteorologique de la France |
| Annuaire Mines Russie | Annuaire du Journal des Mines de Russie |
| Anthropol. (Paris) | Materiaux pour l'Histoire de l'Homme. Revue d'Anthropologie. Revue d'Ethnographie reunis. |
| Anthropol. Congr | See Congr. Int. Anthropol. C. R. |
| Anthropol. Inst. J. | The Journal of the Anthropological Institute of Great Britain and Ireland |

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| Anthropol. Rev. | The Anthropological Review |
| Anthropol. Soc. Mem. | Memoirs read before the Anthropological Society of London |
| Antwerpen, Verh. Genoots. | Verhandelingen van het Genootschap: "Occidit qui non servat" |
| Occ. qui non. | |
| Anvers, Ann. Soc. Med. | Annales de la Societe de Medecine d'Anvers |
| Anvers, Congr. Sci. Geogr. | Compte Rendu du Congres des Sciences Geographiques, Cosmographiques et Commerciales |
| Anvers, J. Pharm. | Journal de Pharmacie, publ. par la Soc. de Pharmacie d'Anvers |
| Apoth. Ztg. | Apotheker Zeitung, Berlin |
| Apothecary | Apothecary, Boston |
| Appreturzeitung | Appreturzeitung |
| Apt, Ann. Soc. Sci. | Annales de la Societe litteraire, scientifique et artistique d'Art (Vaucluse) |
| Aquila | Aquila. A Magyar Ornithologiai Központ Polyoirata. Periodical of Ornithology |
| Arb. Kais. Gesundhts. | Arbeiten aus dem kaiserlichen Gesundheitsamte, Berlin |
| Arb. pharm. Inst., D. Univ. Berlin | Arbeiten aus dem pharmazeutischen Institut der Universität Berlin |
| Arcachon Soc. Sci. Stat. Zool. Trav. | Société Scientifique et Station Zoologique d'Arcachon |
| Arcetri Oss. Pubbl. | See Firenze R. Ist. Pubbl. (Arcetri Oss) |
| Archief Suikerind. | Archief Suikerindustrie in Nederlandsch-Indie |
| Archief Wisk. Genoots. | Archief uitgegeven door het Wiskundig Genootschap |
| Archit. and Eng. | Architect and Engineer |
| Archiv. Agriculturchem. | See Hermbstadt |
| Archiv. Anat. Micro. | Archives d'Anatomie Microscopique |
| Archiv. Anat. Physiol. | Archiv. für Anatomie, Physiologie und wissenschaftliche Medizin |
| Archiv. Anthropol. | Archiv. für Anthropologie... Organ der deutschen Gesellschaft für Anthropologie, Ethnologie und Urgeschichte |
| Archiv. Anthropol. Ethnol. | Archivio per l'Anthropologia e la Etnologia |
| Archiv. Augenheilk. | Archiv. für Augenheilkunde |
| Archiv. Augen- Ohrenheilk. | Archiv. für Augen- und Ohrenheilkunde |
| Archiv. belges méd. mil. | Archives belges de médecine militaire |
| Archiv. Biol. | Archives de Biologie |
| Archiv. Bot. Nord. France | Archives Botaniques du Nord de la France |
| Archiv. Chem. Mikros. | Archiv. Chemie und Mikroskopie |
| Archiv. Cosmol. | Archives cosmologiques. Revue des Sciences Naturelles, avec leurs applications a la Medecine, a l'Agriculture, aux Arts, et a l'Industrie |
| Archiv. Dent. | Archives of Dentistry: A record of Dental knowledge; medical, surgical, microscopical, chemical, and mechanical |
| Archiv. Elect. | Archives de l'Electricite |
| Archiv. Entwickl. Organ. | Archiv. für Entwicklungsmechanik der Organismen |
| Archiv. exper. Path. Pharm. | Archiv. für experimentelle Pathologie und Pharmacologie |
| Archiv. Farmacol. sper. Roma | Archivio di Farmacologia sperimentale e Scienze affini Roma |
| Archiv. fisiol. | Archivio di fisiologia |
| Archiv. gen. Med. | Archives generales de Medecine |
| Archiv. ges. Physiol. | Archiv. für die gesammte Physiologie des Menschen und der Thiere (Pflüger) |
| Archiv. Heilk. | Archiv der Heilkunde |

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| Archiv. Hyg. | Archiv. für Hygiene |
| Archiv. Internal Med. | Archives of Internal Medicine |
| Archiv. intl. pharmacodyn. | Archives internationales de pharmacodynamie et de thereapie |
| Archiv. Ital. Biol. | Archives Italiennes de Biologie. Revues, Résunés Reproductions des Travaux Scientifiques Italiens |
| Archiv. Kinderheilk. | Archiv. für Kinderheilkunde |
| Archiv. Math. Naturvid. | Archiv. for Mathematik og Naturvidenskab |
| Archiv. Math. Phys. | Archiv. der Mathematik und Physik |
| Archiv. Med. | Archives of Medicine |
| Archiv. Med. comparee. | See Rayer |
| Archiv. med. exp. | Archives de medicine experimentale et d'anatomie pathologique |
| Archiv. Med. Navale | Archives de Medecine Navale (et Coloniale) |
| Archiv. Med. Pharm. Militair. | Archives de Medecine et de Pharmacie Militaires |
| Archiv. Mikro. Anat. | Archiv. für Mikroskopische Anatomie (und Entwicklungsgeschichte) |
| Archiv. Miss. Sci. | Archives des Missions Scientifiques et Litteraires |
| Archiv. Naturgesch. | Archiv. für Naturgeschichte |
| Archiv. Naturk. (Dorpat) | Archiv. für die Naturkunde Liv-, Ehst- und Kurlands. Herausgegeben von der Dorpater Naturforscher-Gesellschaft |
| Archiv. Neerland. | Archives Neerlandaises des Sciences Exactes et Naturelles publiees par la Societe Hollandaise des Sciences a Harlem |
| Archiv. Ohrenheilk. | Archiv. für Ohrenheilkunde |
| Archiv. Ophthalm. | Albrecht von Graefe's Archiv für Ophthalmologie |
| Archiv. Ophthalm. Otol. | Archives of Ophthalmology and Otology |
| Archiv. Otol. | Archives of Otology |
| Archiv. Parasit. | Archives de Parasitologie |
| Archiv. path. Anat. | Archiv für pathologische Anatomie und Physiologie und für klinische Medizin (Virchow's) |
| Archiv. Pharm. | Archiv. der Pharmacie; Archiv des Apothekervereins im nördlichen Deutschland. |
| Archiv. Pharm. og Chemi | Archiv. de Pharmaci og Chemi, Copenhagen |
| Archiv. Physiol. | Archives de Physiologie Normale et Pathologique |
| Archiv. Psychiatr. | Archiv. für Psychiatrie und Nervenkrankheiten |
| Archiv. Sci. | Archives of Science and Transactions of the Orleans County Society of Natural Sciences |
| Archiv. sci. med. | Archivio per les scienze mediche |
| Archiv. Sci. Phys. Nat. | Bibliothèque Universelle. Archives des Sciences Physiques et Naturelles |
| Archiv. Sci. Pract. Med. | Archives of Scientific and Practical Medicine |
| Archiv. Slaves Biol. | Archives Slaves de Biologie |
| Archiv. Verdaunungs-krankh. | Archiv. für Verdaunungs-krankheiten |
| Archiv. Wiss. Heilk. | Archiv. des Vereins für gemeinschaftliche Arbeiten zur Förderung der wissenschaftlichen Heilkunde |
| Archiv. Wiss. Prakt. Thierheilk. | Archiv. für wissenschaftliche und praktische Thierheilkunde |
| Archiv. Zool. Anat. Fis. | Archivio per la Zoologia, l'Anatomia, e la Fisiologia |
| Archiv. Zool. Exper. | Archives de Zoologie Experimentale et Generale |
| Arcueil, Mem. Phys. | Memoires de Physique et de Chimie de la Societe d'Arcueil |
| Argent. Inst. Geogr. Bol. | Boletin del Instituto Geografico Argentino |
| Argent. P. | Argentine Patent |
| Argent. Soc. Ci. An. | Anales de la Sociedad Cientifica Argentina |

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| Arkiv. Kemi, Mineral. Geol. | Arkiv för Kemi, Mineralogi och Geologi |
| Arkiv. Math. Astron. Fysik | Arkiv för Mathefnatik Astronomi och Fysik |
| Armagh Nat. Hist. & Phil. Soc. | See Irish Natlist. |
| Arms and Expl. | Arms and Explosives |
| Arnhem, Natuurk. | Natuurkunde. Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Natuurlijke Historie en Litteratuur, uitgegeven van wege het Genootschap: <i>Tot nut en vergenoegen</i> , te Arnhem |
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| Arras, Mem. Acad. | Memoires de l'Academie d'Arras |
| Arras, Mem. Soc. Roy. | Memoires de la Societe Royale d'Arras |
| Art. J. | The Art Journal |
| Artiz. | The Artizan (London) |
| Artus, Jahr. ökon. Chemie | Jahrbuch für ökonomische Chemie, etc. |
| Artus, Vierteljahresschrift | Vierteljahresschrift für technische Chemie, Landwirtschaftliche Gewerbe, Fabrickwesen und Gewerbetreibende überhaupt. |
| Ashmol. Soc. Proc. | Abstracts of the Proceedings of the Ashmolean Society |
| Asiat. Researches | Asiatic Researches; or Transactions, of the (Bengal) Society |
| Asiot. Soc. J. | Journal of the Royal Asiatic Society |
| Assoc. Franc. Compt. rend. | Association Francaise pour l'avancement des Sciences. Comptes Rendus |
| Assoc. Med. J. | See Med. Assoc. Journ. |
| Assur. Mag. | The Assurance Magazine (and Journal of the Institute of Actuaries) |
| Astron. Nachr. | Astronomische Nachrichten |
| Astron. Soc. Mem. | Memoirs of the Astronomical Society of London |
| Astron. Soc. Month. Not. | Monthly Notices of the Astronomical Society of London |
| Astrophys. J. | Astrophysical Journal |
| Atelier Phot. | Atelier des Photographen |
| Ateneo Ital. | L'Ateneo Italiano |
| Athenes Obs. Nat. Ann. | Annales de l'Observatoire National d'Athenes |
| Atlantis | The Atlantis, or Register of Literature and Science |
| Atti. Accad. Ital. | Atti dell'Accademia Italiana di Scienze |
| Atti. accad. Lincei | Atti della reale accademia dei Lincei, rendiconti, classe di scienze fisiche, matematiche e naturali |
| Atti. Coll. Ing. Archit | Atti de Collegio degli Ingegneri ed Architetti in Milano |
| Atti. inst. incoragg. | Atti del R. istituto d'incoraggiamento di Napoli, Naples, Italy |
| Atti. R. Accad. Sci. Torino | Atti della Reale Accademia della Scienze di Torino |
| Atti Sci. Ital. | Riunione degli Scienziati Italiani |
| Atti Soc. Elvet. | Atti della Societa Elvetica delle Scienze Naturali |
| Aube, Mem. Soc. Agric. | Memoires de la Societe d'Agriculture, des Sciences, et des Lettres du department de l'Aube |
| Augsb. Naturhist. Ver. Ber. | Berichte des Naturhistorischen Vereins in Augsburg |
| Auk | The Auk. A Quarterly Journal of Ornithology |
| Ausland | Das Ausland |
| Aust. P. | Austrian Patent |
| Aust.-Hung. P. | Austro-Hungarian Patent |
| Australasian Assoc. Rep. | Report of the... Meeting of the Australasian Association for the Advancement of Science |
| Australasian J. Pharm. | Australasian Journal of Pharmacy, Melbourne |
| Australian Med. J. | Australian Medical Journal |

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| Australia Med. Rec. | Medical Records of Australia |
| Australian P. | Australian P. |
| Australian Sugar J. | Australian Sugar Journal |
| Autun, Mem. Soc. Eduenne | Memoires de la Societe Eduenne |
| Auvergne, Ann. Sci. | Annales Scientifiques, Litteraires, et Industrielles de l'Auvergne |
| Auxerre, Bull. Soc. Sci. | Bulletin de la Societe des Sciences Historiques et Naturelles de l'Yonne |
| Badischen Aerzt. Verein. Mitth. | Mittheilungen des Badischen ärztlichen Vereins |
| Bah. P. | Bahamas Patent |
| Ballenstedt, Archiv. | Archiv für die neuesten Entdeckungen aus der Urwelt |
| Ballot, Mag. Landbouw. | Magazin voor Landbouw en Kruidkunde |
| Baltimore Med. Phys. Recorder | Baltimore Medical and Physical Recorder |
| Bamb. Naturf. Ges. Ber. | Bericht der naturforschenden Gesellschaft zu Bamberg |
| Barb. P. | Barbados Patent |
| Barcelona Acad. Bol. | Boletin de la Real Academia de Ciencias y Artes de Barcelona |
| Barcelona Acad. Mem. | Memorias de la Real Academia de Ciencias Naturales y Artes de Barcelona |
| Barrow Field Club Report | Barrow Naturalists' Field Club and Literary and Scientific Association. Annual Report and Proceedings |
| Basel, Ber. | Bericht über die Verhandlungen der Naturforschenden Gesellschaft in Basel |
| Batavia Genootsch. Verh. | Verhandlingen van het Bataviaasch Genootschap der Kunsten en Wetenschappen |
| Batavia, Natuur. Archief. | Natuur- en Geneeskundig Archief voor Nederlandsch-Indië |
| Batavia, Natuurk. Tijdschr. | Natuurkundig Tijdschrift voor Nederlandsch-Indië, uitgegeven door de Koninklijke Natuurkundige Vereeniging in Nederlandsch-Indië |
| Batavia, Notulen | Notulen van de Algemeene en Bestuurs-Vergaderingen van het Bataviaasch Genootschap van Kunsten en Wetenschappen |
| Batavia Obs. Obsns. | Observations made at the (Royal) Magnetical and Meteorological Observatory at Batavia |
| Batavia, Tijdschr. | Tijdschrift voor Indische Taal-, Land-, en Volkenkunde |
| Batavia, Verh. Natuurk. Vereen. | Verhandlingen der Natuurkundige Vereeniging in Nederlandsch-Indië |
| Bath Micro. Soc. Minutes | Extracts from the Minutes of the Bath Microscopical Society |
| Bath Natur. Hist. Club. Proc. | Proceedings of the Bath Natural History and Antiquarian Field Club |
| Bath Soc. Agric. Letters | Letters and Papers of the Bath and West of England Society for the Encouragement of Agriculture, Arts, Manufactures, and Commerce |
| Baugew. Ztg. | Baugewerks-Zeitung |
| Baumgartner Zts. | Zeitschrift für Physik, Mathematik, und verwandte Wissenschaften |
| Bayer. Gewerbeztg. | Bayerische Gewerbezeitung |
| Bayer. Kunst. Gewerbebl. | Kunst und Gewerbeblatt (Polytechn. Verein Königreich Bayern) |
| Bayer, Landw. Ver. Erg. | Ergebnisse landwirtschaftlicher und agrikulturchemischer Versuche an der Station des General-Comite des Bayerischen Landwirtschaftlichen Vereines in München |

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| Bayeux, Mem. Soc. Agric. | Memoires de la Societe d'Agriculture, Sciences, Arts, et Belles-Lettres de Bayeux |
| Bd. Trade J. | Board of Trade Journal |
| Beauvais, Soc. Acad. Mem. | Memoires de la Societe Academique d'Archeologie, Sciences et Arts du Departement de l'Oise |
| Beitr. Anat. Physiol | See Eckhard |
| Beitr. Anthropol. Bayerns | Beiträge zur Anthropologie und Urgeschichte Bayerns. Organ der Münchener Gesellschaft für Anthropologie, Ethnologie und Urgeschichte |
| Beitr. Biol. Pflanz. | Beiträge zur Biologie der Pflanzen |
| Beitr. Geophys. | Beiträge zur Geophysik. Abhandlungen aus dem Geographischen Seminar der Universität Strassburg. Beiträge zur Geophysik. Zeitschrift für Physikalische Erdkunde |
| Beitr. Kryptog. Schweiz | Beiträge zur Kryptogamenflora der Schweiz |
| Beitr. Mecklenb. Aerzte | Beiträge Mecklenburgischer Aerzte zur Medicin und Chirurgie |
| Beitr. Morphol. | Beiträge zur Morphologie und Morphogenie. Untersuchungen aus dem Anatomischen Institut zu Erlangen |
| Beitr. Naturk. Preussens | Beiträge zur Naturkunde Preussens. Herausgegeben von der Königlichen Physikalisch-Oekonomischen Gesellschaft zu Königsberg |
| Beitr. Paläont. Oesterr.-Ung. | Beiträge zur Paläontologie Oesterreich-Ungarns und des Orients |
| Beitr. Path. Anat. | Beiträge zur Pathologischen Anatomie und Physiologie. Beiträge zur Pathologischen Anatomie und zur Allgemeinen Pathologie |
| Beitr. Physiol. Morphol. | Beiträge zur Physiologie und Morphologie Niederer Organismen. |
| Beitr. Russ Reich. | Beiträge zur Kenntniss des Russischen Reiches und der angrenzenden Länder Asiens |
| Belfast, Clin. Soc. Trans. | Transactions of the Clinical and Pathological Society of Belfast |
| Belfast Field Club Rep. | Annual Reports and Proceedings of the Belfast Naturalists' Field Club |
| Belfast Natur. Hist. Soc. Proc. | Proceedings of the Belfast Natural History and Philosophical Society |
| Belg. Horticole | La Belgique Horticole. Annales de Botanique et d'Horticulture |
| Belg. P. | Belgian Patent |
| Bengal Asiat. Soc. J. | Journal of the Asiatic Society of Bengal |
| Bengal Asiat. Soc. Proc. | Proceedings of the Asiatic Society of Bengal |
| Bengal Govt. Records | Selections from the Records of the Bengal Government |
| Bengal, Phot. Soc. J. | Journal of the Photographic Society of Bengal |
| Ber. | Berichte der Deutschen Chemischen Gesellschaft, Berlin |
| Ber. deut. bot. Ges. | Berichte der deutschen botanischen Gesellschaft |
| Ber. pharm. Ges. | Berichte der deutschen pharmazeutischen Gesellschaft |
| Ber. phys. Ges. | Berichte der deutschen physikalischen Gesellschaft |
| Ber. Sächs. Ges. Wiss. | Berichte über die Verhandlungen der Königl. Sächs. Gesellschaft der Wissenschaften zu Leipzig |
| Ber. Veter. König. Sach. | Berichte über das Veterinärwesen im Königreich Sachsen |
| Berg. Hüttenm. Jahr. | Berg- und hüttenmannisches Jahrbuch |
| Berg. Hüttenm. Ztg. | Berg- und hüttenmannische Zeitung |

XXXVI . . . LIST OF ABBREVIATIONS TO LITERATURE . . .

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| Bergens Mus. Aarb. | Bergens Museums Aarbog for . . . Afhandlinger og Aarsberetning udgivne af Bergens Museum |
| Berggeist | Der Berggeist |
| Berghaus, Ann. | Annalen der Erd-, Völker- und Staatenkunde |
| Berghaus, Zts. Erdk. | Zeitschrift für vergleichende Erdkunde |
| Berlin Afrik. Ges. Mitth. | Mittheilungen der Afrikanischen Gesellschaft in Deutschland |
| Berlin Akad. Abh. | Abhandlungen der k. Akademie der Wissenschaften zu Berlin |
| Berlin Akad. Monatsber. | Monatsberichte der k. Preussischen Akademie der Wissenschaften zu Berlin |
| Berlin Akad. Sitzber. | Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin |
| Berlin Ann. Telegr. | Annalen der Telegraphie |
| Berlin Astron. Jahr. | Berliner Astronomisches Jahrbuch |
| Berlin Bot. Gartens Jahr. | Jahrbuch des Königlichen Botanischen Gartens und des Botanischen Museums zu Berlin |
| Berlin Bot. Gartens Notizbl. | Notizblatt des Königl. Botanischen Gartens und Museums zu Berlin |
| Berlin Ent. Ges. | See Ill. Wschr. Ent. |
| Berlin Entom. Zts. | Berliner Entomologische Zeitschrift; herausg. von dem Entomologischen Verein in Berlin |
| Berlin Ges. Anthrop. Verh. | See Ztschr. Ethnol. |
| Berlin Ges. Erdk. Verh. | Verhandlungen der Gesellschaft für Erdkunde zu Berlin |
| Berlin Ges. Erdk. Zts. | See Berlin Zts. Erdk. |
| Berlin Ges. Geburtshlf. Gynäk. | See Zts. Geburtshlf. Gynäk. |
| Berlin Ges. Naturf. Freunde Mag. | Magazin der Gesellschaft Naturforschender Freunde zu Berlin, für die neuesten Entdeckungen in der gesammten Naturkunde |
| Berlin Ges. Naturf. Freunde N. Schr. | Neue Schriften der Gesellschaft Naturforschender Freunde in Berlin |
| Berlin Ges. Naturf. Freunde Verh. | Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin |
| Berlin Ges. Psychiatr. | See Arch. Psychiatr. |
| Berlin Gesundheitsamt Biol. Abth. Arb. | Arbeiten aus der Biologischen Abtheilung für Land- und Forstwirtschaft am Kaiserlichen Gesundheitsamte |
| Berlin Ind. Ztg. | Industrie Zeitung, Berlin |
| Berlin Jahr. Pharm. | Berlinisches Jahrbuch für die Pharmacie und für die damit verbundenen Wissenschaften |
| Berlin Klin. Wochenschr. | Berliner klinische Wochenschrift |
| Berlin Mem. Acad. | Memoires de l'Academie Royale des Sciences de Berlin |
| Berlin Mitth. Ges. Naturf. | Mittheilungen aus den Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin |
| Berlin Monatsber. | Monatsberichte der K. Preuss. Akademie der Wissenschaften zu Berlin |
| Berlin Monatsber. Ges. Erdk. | Monatsberichte über die Verhandlungen der Gesellschaft für Erdkunde zu Berlin |
| Berlin Naturf. Freunde Sitzber. | Sitzungs-Berichte der Gesellschaft Naturforschender Freunde zu Berlin |
| Berlin Neue Zts. Geburtsk. | Neue Zeitschrift für Geburtskunde |
| Berlin Physiol. Ges. Verh. | See Arch. Anat. Physiol |
| Berlin Physik. Reichsanst. Abh. | Wissenschaftliche Abhandlungen der Physikalisch Technischen Reichsanstalt |
| Berlin Verh. Med. Ges. | Verhandlungen der Berliner medicinischen Gesellschaft |

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| Berlin Zool. Mus. Mitth. | Mittheilungen aus der Zoologischen Sammlung des Museums für Naturkunde in Berlin |
| Berlin Zts. Erdk. | Zeitschrift der Gesellschaft für Erdkunde zu Berlin |
| Berlin Mitth. | Mittheilungen der Naturforschenden Gesellschaft in Bern |
| Berwick Natur. Club Hist. | History of the Berwickshire Naturalists' Club |
| Berz. Jahr. Chem. | Berzelius Jahresberichte der Chemie |
| Besancon, Mem. Soc. Emul. | Mémoires et Comptes Rendus de la Société (Libre) d'Émulation du Doubs |
| Besancon, Seances Publ. | Seances publiques de l'Académie des Sciences, Arts, et Belles-Lettres de Besancon |
| Beton Eisen | Beton und Eisen |
| Betterave | Betterave |
| Beziere Soc. Sci. Bull. | Bulletin de la Société d'Étude des Sciences Naturelles de Beziere |
| Bianconi, Rep. Ital. | Repertorio Italiano Per la Storia Naturale |
| Bibl. Anat. | Bibliographie Anatomique. Revue des Travaux en langue française. Anatomie. Histologie. Embryologie. Anthropologie |
| Bibl. Bot. | Bibliotheca Botanica. Abhandlungen aus dem Gesamtgebiete der Botanik |
| Bibl. Brit. | Bibliothèque Britannique, ou Recueil extrait des Ouvrages Anglais periodiques et autres; partie des Sciences et Arts |
| Bibl. Ital. | Giornale dell' I. R. Istituto Lombardo di Scienze, Lettere ed Arti, e <i>Biblioteca Italiana</i> |
| Bibl. Math. | Bibliotheca Mathematica. Zeitschrift für Geschichte der Mathematik. Journal d'Histoire des Mathématiques. Bibliotheca Mathematica. Zeitschrift für Geschichte der mathematischen Wissenschaften |
| Bibl. Univ. | Bibliothèque Universelle des Sciences, Archives des Sciences Physiques et Naturelles |
| Bibl. Zool. | Bibliotheca Zoologica |
| Bied. Zentr. | Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb |
| Bierbrauer | Der Bierbrauer |
| Bijdr. tot de Dierkunde | Bijdragen tot de Dierkunde |
| Biochem. Bull. | Biochemical Bulletin |
| Biochem. J. | The Bio-Chemical Journal |
| Biochem. Zentr. | Biochemisches Zentralblatt, Leipzig |
| Biochem. Zts. | Biochemische Zeitschrift |
| Biol. Bull. | Biological Bulletin |
| Biol. Zentr. | Biologisches Zentralblatt |
| Biophys. Zentr. | Biophysikalisches Zentralblatt, Leipzig |
| Birmingham Natur. Hist. & Micro. Soc. Trans. | See Midland Natlist Trans. |
| Birmingham Phil. Soc. Proc. | Proceedings of the Birmingham Philosophical Society |
| Blankenburg, Ber. | Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg |
| Blätter Blech-Arb. | Deutsche Blätter für Blecharbeiter |
| Blätter Kunstgew. | Blätter für Kunstgewerbe |
| Blätter Zuckerrüb. | Blätter für Zuckerrübenbau |
| Bleekrode, Nieuw Tijdschrift | Nieuw Tijdschrift gewijd aan alle takken van Volkswijst, Nijverheid, Landbouw, Mijnwezen, Handel, Spoorwegen, Telegraphie en Scheepvaart |
| Blois, Mem. Soc. Sci. | Mémoires de la Société des Sciences et des Lettres de Blois |
| Blois, Soc. Loir et Cher Mem. | Mémoires de la Société des Sciences et Lettres de Loir et Cher |

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| Boerhaave | Boerhaave |
| Böhm. Ges. Akh. | Abhandlungen der Königlich Böhmischen Gesellschaft der Wissenschaften |
| Böhm. Ges. Wiss. Jahr. | Jahresbericht der königl. böhm. Gesellschaft der Wissenschaften |
| Böhm. Monatschr. Ges. Mus. | Monatschrift der Gesellschaft des Vaterländischen Museums in Böhmen |
| Bol. P. | Bolivia Patent |
| Boll. chim. farm. | Bolletino chimico farmaceutico, Milan |
| Boll. estac. agr. Ciudad Juarez | Boletin de la estacion agricola experimental de Ciudad Juarez |
| Boll. ingen. | Boletin de ingenieros |
| Boll. Natur. Siena | Bollettino del Naturalista Collettore, Allevatore, Coltivatore |
| Bologna Accad. Sci. Mem. | Memorie della (R.) Accademi delle Scienze dell' Istituto di Bologna |
| Bologna, Mem. Inst. Naz. Ital. | Memorie dell'Istituto Nazionale Italiano |
| Bologna, Mem. Soc. Med. | Memorie della Societa Medica di Bologna |
| Bologna, Mem. Soc. Med. Chir. | Memorie della Societa Medico-chirurgica di Bologna |
| Bologna, Nov. Comment. | Novi Commentarii Academiae Scientiarum Instituti Bononiensis |
| Bologna, Opusc. | Opuscoli della Societa Medico-chirurgica di Bologna |
| Bologna, Opusc. Sci. | Opuscoli Scientifici |
| Bologna, Opusc. Sci. N. Coll. | Nuova collezione d'Opuscoli Scientifici |
| Bologna Rend. | Rendiconto delle Sessioni dell' Accademia Reale delle Scienze dell' Istituto di Bologna |
| Bombay, Agric. Hort. Soc. Proc. | Proceedings of the Agricultural and Horticultural Society of Western India |
| Bombay Govt. Records | Selections from the Records of the Bombay Government |
| Bombay, Med. Phys. Soc. Trans. | Transactions of the Medical and Physical Society of Bombay |
| Bombay Natur. Hist. Soc. J. | The Journal of the Bombay Natural History Society |
| Bombay, Roy. Asiat. Soc. J. | The Journal of the Bombay Branch of the Royal Asiatic Society |
| Bone, Acad. Hippone Bull. | Bulletin de l'Academie d'Hippone |
| Bonn, Corresp. Blatt Nat. Hist. Ver. | Correspondenzblatt des Naturhistorischen Vereins für Rheinland und Westphalen |
| Bonn, Niederrhein. Ges. Sitzber. | Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn |
| Bonn, Untersuch. Physiol. Lab. | Untersuchungen aus dem physiologischen Laboratorium zu Bonn |
| Bonn, Verh. Naturhist. Ver. | Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens |
| Bonplandia | Bonplandia |
| Bordeaux, Acad. Sci. Seances Publ. | Seances publiques de l'Academie Royale des Sciences, Belles-Lettres, et Arts de Bordeaux |
| Bordeaux, Actes Acad. Sci. | Recueil des Actes de l'Academie des Sciences, Belles-Lettres, et Arts de Bordeaux |
| Bordeaux, J. Med. | Journal de Medecine de Bordeaux |
| Bordeaux, J. Med. Prat. | Journal de Medecine pratique, ou Recueil des Travaux de la Société de Medecine de Bordeaux |
| Bordeaux, Mem. Soc. Med. Chir. | Memoires et Bulletins de la Société Medico-Chirurgicale des Hopitaux et Hospices de Bordeaux |
| Bordeaux, Mem. Soc. Sci. Phys. | Memoires de la Société des Sciences Physiques et Naturelles de Bordeaux |

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| Bordeaux, Soc. Linn. Actes | Actes de la Société Linneenne de Bordeaux |
| Bordeaux, Soc. Linn. Bull. | Bulletin d'Histoire Naturelle de la Société Linneenne de Bordeaux |
| Bordeaux, Soc. Med. Mem. | Memoires et Bulletins de la Société de Médecine et de Chirurgie de Bordeaux |
| Bordeaux, Soc. Sci. P.-V. | Procès-Verbaux des Séances de la Société des Sciences Physiques et Naturelles de Bordeaux |
| Bornemann, Der Ingenieur | Der Ingenieur |
| Boston J. Phil. | The Boston Journal of Philosophy and the Arts |
| Boston J. Natur. Hist. | Boston Journal of Natural History |
| Boston Med. Surg. J. | Boston Medical and Surgical Journal |
| Boston, Mem. Amer. Acad. | Memoirs of the American Academy of Arts and Sciences |
| Boston, Mem. Natur. Hist. Soc. | Memoirs read before the Boston Society of Natural History |
| Boston Pap. Soc. Natur. Hist. | Occasional papers of the Boston Society of Natural History |
| Boston, Proc. Natur. Hist. Soc. | Proceedings of the Boston Society of Natural History |
| Boston Soc. Med. Sci. J. | Journal of the Boston Society of Medical Sciences |
| Bot. Centr. | Botanisches Centralblatt. Referirendes Organ für das Gesamtgebiet der Botanik des In- und Auslandes |
| Bot. Centr. Beihefte | Beihefte zum Botanischen Centralblatt |
| Bot. Cong. Proc. | The International Horticultural Exhibition and Botanical Congress: Report of Proceedings |
| Bot. Gaz. | The Botanical Gazette |
| Bot. Jahr. (Engler) | Botanische Jahrbücher, Engler, Leipzig |
| Bot. Mag., Tokyo | The Botanical Magazine, Tokyo |
| Bot. Notiser | Botaniska Notiser |
| Bot. Tidsskr. | Botanisk Tidsskrift udgivet af den Botaniske Forening i Kjøbenhavn |
| Bot. Untersuch. | Botanische Untersuchungen aus dem Physiologischen Laboratorium der landwirthschaftlichen Lehranstalt in Berlin |
| Bot. Untersuch. (Brefeld's) | Untersuchungen aus dem Gesamtgebiete der Mykologie |
| Bot. Ver. Gesamtthüringen | See Jena Geogr. Ges. Mitth. |
| Botan. Ztg. | Botanische Zeitung |
| Bot. Zentr. | Botanisches Zentralblatt |
| Botaniste | Le Botaniste |
| Bouchardat, Archiv. | Archives de Physiologie, de Therapeutique, et d'Hygiène |
| Boue, J. Geol. | Journal de Geologie |
| Boulogne, Mem. Soc. Agric. | Memoires de la Société d'Agriculture, etc., de Boulogne-sur-Mer |
| Bourse cuirs Liege | Bourse aux cuirs de Liege, bulletin hebdomadaire |
| Brandenb. Bot. Ver. Verh. | Verhandlungen des botanischen Vereins für die Provinz Brandenburg |
| Brass World | Brass World and Platers Guide, The |
| Braunk. | Braunkohle |
| Braunschw. Ver. Naturwiss. Jahr. | Jahresbericht des Vereins für Naturwissenschaft zu Braunschweig |
| Braz. P. | Brazilian Patent |
| Bremen Abh. | Abhandlungen herausgegeben vom Naturwissenschaftlichen Verein zu Bremen |
| Brenn. Ztg. | Brennerei Zeitung |
| Brera, Giorn. Med. Prat. | Giornale di Medicina Pratica |
| Brera, Nuovi Comment. | Nuovi Commentari di Medicina |

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| Brescia, Comment. Ateneo | Commentarij della Accademia di Scienze, Lettere, ed dell'Ateneo di Brescia |
| Breslau, Ann. Klin. Inst. | Annalen des Klinisch-chirurgischen Instituts auf der Universität zu Breslau |
| Breslau, Bot. Garten.Arb. | Arbeiten aus dem Königl. Botanischen Garten zu Breslau |
| Breslau, Gewerbebl. | Breslauer Gewerbeblatt |
| Breslau, Jahr. Schles. Ver. | Jahrbuch des Schlesischen Vereins für Berg- und Hüttenwesen |
| Breslau, Schles. Ges. Jahr. | Jahresbericht des Akademischen Naturwissenschaftlichen Vereins zu Breslau |
| Breslau, Studien Physiol. Inst. | Studien des Physiologischen Instituts zu Breslau |
| Breslau, Zts. Klin. Med. | Zeitschrift für Klinische Medicin |
| Brest Soc. Acad. Bull. | Bulletin de la Société Académique de Brest |
| Brewers J. (Lon.) | Brewers Journal and Hop and Malt Trades Review, The (London) |
| Brewers J., N. Y. | Brewers Journal, New York |
| Brick | Brick |
| Brick J. | Brick, Pottery and Glass Journal |
| Brick and Clay Record | Brick and Clay Record |
| Brighton, Proc. Natur. Hist. Soc. | Reports and Abstracts of the Proceedings of the Brighton and Sussex Natural History Society |
| Bristol Proc. Nat. Soc. | Proceedings of the Bristol Naturalists' Society |
| Brit. Assoc. Rep. | Report of the Meetings of the British Association for the Advancement of Science |
| Brit. Clay Worker | British Clay Worker, The |
| Brit. Food J. | British Food Journal |
| Brit. For. Med. Chir. Rev. | British and foreign Medico-Chirurgical Review |
| Brit. Inst. Publ. Health | See J. State Med. |
| Brit. J. Almanac | British Journal of Photography Almanac |
| British J. Dent. Sci. | The British Journal of Dental Science |
| Brit. J. Phot. | British Journal of Photography |
| Brit. Med. J. | British Medical Journal |
| Brit. Mycol. Soc. Trans. | The British Mycological Society. Transactions |
| Brit. Pharm. Confer. Proc. | Proceedings of the British Pharmaceutical Conference |
| Brit. Pharm. Confer. Trans. | Year Book of Pharmacy, comprizing Abstracts of Papers. With the Transactions of the British Pharmaceutical Conference |
| Brit. Colon. Drug. | British and Colonial Druggist, London |
| Brit. Guiana Agr. Soc. | See Timchri |
| Brit. Guiana P. | British Guiana Patent |
| Brit. Hond. P. | British Honduras Patent |
| Brooklyn Entom. Soc. Bull. | Bulletin of the Brooklyn Entomological Society |
| Brosche, Zts. | Zeitschrift für Natur- und Heilkunde |
| Broussais, Anh. | Annales des la Medicine Physiologique |
| Brown-Sequard, J. Physiol. | Journal de la Physiologie de l'Homme et des Animaux |
| Brugnattelli, Giorn. | Giornale di Fisica, Chimica, e Storia Naturale |
| Brünn Verh. | Verhandlungen des Naturforschenden Vereines in Brünn |
| Brux. Acad. Bull. | Bulletins de l'Academie Royale des Sciences, etc., de Belgique |
| Brux. Acad. Cent. Anniv. | Centieme Anniversaire de Foundation de l'Academie Royale de Belgique |
| Brux. Acad. Med. Belg. Bull. | Bulletin de l'Academie Royale de Medecine Belgique |
| Brux. Acad. Sci. Mem. | Nouveaux memoires de l'Academie Royale, des Sciences et Belles-lettres de Bruxelles |

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| Brux. Actes Soc. Med. | Actes de la Société Médicale de Bruxelles |
| Brux. Ann. Soc. Entom. Belge | Annales de la Société Entomologique Belge |
| Brux. Ann. Soc. Malacol. | Annales de la Société Malacologique de Belgique |
| Brux. Ann. Trav. Pub. | Annales des Travaux Publics de Belgique |
| Brux. Ann. Univ. Belg. | Annales des Universités de Belgique |
| Brux. Bull. Belge Phot. | Bulletin Belge de la Photographie |
| Brux. Bull. Soc. Bot. | Bulletins de la Société Royale de Botanique de Belgique |
| Brux. Congr. Bot. Act. | Actes du Congrès de Botanique horticole réuni à Bruxelles |
| Brux. Congr. Bot. (C. R.) | Congrès de Botanique et d'Horticulture de 1880 tenu à Bruxelles |
| Brux. J. Med. | Journal de Médecine, de Chirurgie, et de Pharmacologie |
| Brux. J. Soc. Centr. Agric. | Journal de la Société Centrale d'Agriculture de Belgique |
| Brux. Mem. Couronn. | Mémoires Couronnées et Mémoires des Savants Étrangers |
| Brux. Mus. Congo Ann. | État Indépendant du Congo. Annales du Musée du Congo, publiées par ordre du Secrétaire d'État |
| Brux. Mus. Hist. Natur. Ann. | Annales du Musée Royal d'Histoire Naturelle de Belgique |
| Brux. Mus. Hist. Natur. Bull. | Bulletin du Musée Royal d'Histoire Naturelle de Belgique |
| Brux. Mus. Hist. Natur. Mem. | Mémoires du Musée Royal d'Histoire Naturelle de Belgique |
| Brux. Soc. Agric. Journ. | Journal de la Société Centrale d'Agriculture de Belgique |
| Brux. Soc. Belge Micro. Ann. | Annales de la Société Belge de Microscopie |
| Brux. Soc. Belge Micro. Bull. | Bulletin (des Séances) de la Société Belge de Microscopie |
| Brux. Soc. Entom. Ann. | Annales de la Société Entomologique de Belgique |
| Brux. Soc. Entom. Mem. | Mémoires de la Société Entomologique de Belgique |
| Brux. Soc. Linn. Bull. | Bulletin de la Société Linnéenne de Bruxelles |
| Brux. Soc. Sci. | See Rev. Qu'est. Sci. |
| Brux. Soc. Sci. Ann. | Annales de la Société Scientifique de Bruxelles |
| Bucarest. Acad. Rom. Anal. | Analele Academiei Române |
| Bucarest Soc. Sci. Bul. | Buletinul Societății de Științe (Fizice, Fixice, Chimia și Mineralogia) din Bucuresci-Romania. Bulletin de la Société des Sciences, Bucarest-Roumanie |
| Buchholz | See Annab.-Buchh. Ver. Nat. Jber. |
| Buda, Evkönyvei | A' Magyar Tudós Társaság' Evkönyvei (Year Books of the Hungarian Scientific Association) |
| Buda, Pályamunkák. | Természettudományi Pályamunkák |
| Buda, Tudománytar. | Tudománytar Közre bocsátja a' Magyar Tudós Társaság |
| Buffalo Bull. | Bulletin of the Buffalo Society of Natural Sciences |
| Builder | The Builder |
| Buitenzorg Inst. Bot. Bull. | 's Lands Plantentuin. Bulletin de l'Institut Botanique de Buitenzorg |
| Buitenzorg Jard. Bot. Ann. | Annales du Jardin Botanique de Buitenzorg |
| Bull. Acad. Med. | Bulletin of the Academy of Medicine |
| Bull. Acad. roy. Belg. | Académie royale de Belgique; Bulletin de la Classe des Sciences |
| Bull. Acad. Sci., Craoow. | Bulletin international de l'Académie des Sciences de Cracovie |

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| Bull. Acad. Sci., Petrograd | Bulletin de l'Académie Impériale des Sciences de Petrograd |
| Bull. Amer. Inst. Min. Eng. | Bulletin American Institute of Mining Engineers |
| Bull. Amer. Pharm. Assoc. | Bulletin of the American Pharmaceutical Association |
| Bull. assoc. chim. suc. dist. | Bulletin de l'association des chimistes de sucrerie distillerie de France |
| Bull. Bur. Agric. | Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases |
| Bull. Bur. Chem. U. S. Dept. Agric. | Bulletins, Bureau of Chemistry, U.S. Department of Agriculture |
| Bull. Bur. Mines | Bureau of Mines Bulletin, Department of the Interior |
| Bull. Bur. Standards | Bulletin of the Bureau of Standards |
| Bull. Col. School Mines | Bulletin of the Colorado School of Mines |
| Bull. Dept. Agric. Jamaica | Bulletin of the Department of Agriculture, Jamaica |
| Bull. Dept. Agric. Trinidad | Bulletin of Agricultural Information, Department of Agriculture, Trinidad |
| Bull. Geol. Inst. Univ. Upsala | Bulletin of the Geological Institute of the University of Upsala |
| Bull. Geol. Soc. Amer. | Bulletin of the Geological Society of America |
| Bull. Hyg. Lab. | Bulletins of the Hygienic Laboratory, United States Public Health and Marine Hospital Service |
| Bull. Imp. Inst. | Bulletin of the Imperial Institute, London |
| Bull. Iron Assoc. | Bulletin of the American Iron and Steel Association |
| Bull. Johns Hopkins Hosp. | Bulletin of Johns Hopkins Hospital |
| Bull. Mass. Inst. Tech. | Bulletin of the Massachusetts Institute of Technology |
| Bull. Med. Belge. | Bulletin Medical Belge. |
| Bull. Musée | Bulletin du Musée de l'industrielle de Belgique |
| Bull. Pharmacie | Bulletin de Pharmacie |
| Bull. Pharmacy | Bulletin of Pharmacy |
| Bull. Pharm. Sud-est | Bulletin de Pharmacie du Sud-est, Montpellier |
| Bull. Sci. France Belg. | Bulletin Scientifique de la France et de la Belgique |
| Bull. Sci. Nord | Bulletin Scientifique, Historique et Littéraire du Département du Nord et des pays voisins |
| Bull. Sci. pharmacolog. | Bulletin des Sciences pharmacologiques |
| Bull. Soc. Bot. France | Bulletin de la Société Botanique de France |
| Bull. Soc. Bot. Belg. | Bulletin de la Société Royale de Botanique de Belgique |
| Bull. Soc. Chim. | Bulletin de la Société Chimique de France |
| Bull. Soc. Chim. Belg. | Bulletin de la Société Chimique de Belgique |
| Bull. Soc. Encourag. | Bulletin de la Société d'Encouragement |
| Bull. Soc. franc. Minéral. | Bulletin de la Société Française de Mineralogie |
| Bull. Soc. franc. Phot. | Bulletin de la Société Française de Photographie |
| Bull. Soc. geol. France | Bulletin de la Société géologique de France |
| Bull. Soc. Ind. Amiens | Bulletin de la société industrielle d'Amiens |
| Bull. Soc. Ind. Marseille | Bulletin de la Société industrielle de Marseille |
| Bull. Soc. Ind. Minérale | Bulletin de la société de l'industrie minérale |
| Bull. Soc. Ind. Mulh. | Bulletin de la société industrielle de Mulhouse |
| Bull. Soc. Ind. Nord | Bulletin mensuel de la société industrielle du Nord |
| Bull. Soc. Ind. Rouen | Bulletin de la société industrielle de Rouen |
| Bull. Soc. internatl. elect. | Bulletin de la Société internationale des electriciens |
| Bull. Soc. Med. Amiens | Bulletin des Travaux de la Société Médicale d'Amiens |
| Bull. Soc. med. Gand | Bulletin de la Société de Médecine de Gand |
| Bull. Soc. Mycol. | Bulletin de la Société Mycologique de France |
| Bull. Soc. pharm. Bord. | Bulletin de la société pharmacie de Bordeaux |
| Bull. Soc. phot. Belg. | Bulletin de la Société photographique de Belgique |
| Bull. Soc. Romane Stiin. | Buletinul societatii Romane de Stiinte |
| Bull. Soc. roy. pharm. | Bulletin de la société de pharmacie de Bruxelles royale |
| Bull. Soc. sci. med. Rennes | Bulletin de la société scientifique et médicale de l'ouest, Rennes |

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| Bull. Soc. vaudoise | Bulletin de la Société vaudoise, des Ingenieurs et des Architectes |
| Bull. Torrey Bot. Club | Bulletin of the Torrey Botanical Club, New York |
| Bull. Vulc. Ital. | Bullettino del Vulcanismo Italiano (e di Geodinamica generale) |
| C. A. | Chemical Abstracts |
| Cabanis, J. Ornithol. | Journal für Ornithologie |
| Cadiz, Period. Mens. Cien. | Periodico mensual de Ciencias matematicas y fisicas |
| Caen, Acad. Mem. | Memoires de l'Academie des Sciences, Belles Lettres, et Arts de Caen |
| Caen, Bull. Soc. Linn. | Bulletin de la Société Linneene de Normandie |
| Normandie | |
| Caen, Mem. Soc. Linn. | Memoires de la Société Linneenne de Normandie |
| Normandie | |
| Caen, Travaux | Precis des Travaux de la Société d'Agriculture, &c. de Caen |
| Calcutta, J. Natur. Hist. | The Calcutta Journal of Natural History |
| Calcutta, Quart. J. | Quarterly Journal of the Medical-Physical Society |
| Calcutta Roy. Bot. Gard. | Annals of the Royal Botanic Garden, Calcutta |
| Ann. | |
| Calcutta, Trans. Med. | Transactions of the Medical and Physical Society of Calcutta |
| Phys. Soc. | |
| Cal. Acad. Bull. | Bulletin of the California Academy of Sciences |
| Cal. Acad. Mem. | Memoirs of the California Academy of Sciences |
| Cal. Acad. Natur. Sci. | Proceedings of the Californian Academy of Natural Sciences |
| Proc. | |
| Cal. Acad. Pap. | Occasional Papers of the California Academy of Sciences |
| Cal. Min. Bur. Bull. | California State Mining Bureau. Bulletin |
| Cal. Min. Bur. Rep. | (California State Mining Bureau). Report of the State Mineralogist |
| Calvados, Mem. Soc. Linn. | Memoires de la Société Linneenne du Calvados |
| Cambrai, Mem. Soc. Emul. | Memoires de la Société d'Emulation de Cambrai |
| Cambridge Mem. Analyt. Soc. | Memoirs of the Cambridge Analytical Society |
| Cambridge Mus. Comp. Zool. Bull. | Proceedings of the Museum of Comparative Zoology at Harvard College, Cambridge, Mass. |
| Cambr. Ornith. Club Bull. | Bulletin of the Nuttall Ornithological Club. A Quarterly Journal of Ornithology |
| Cambridge Phil. Soc. Proc. | Proceedings of the Cambridge Philosophical Society |
| Cambridge Phil. Soc. Trans. | Transactions of the Cambridge Philosophical Society |
| Cambridge, Studies Physiol. Labor | Studies from the Physiological Laboratory in the University of Cambridge |
| Camera Oscura | La Camera Oscura; rivista periodica universale dei progressi della Fotografia |
| Can. | Canadian—Canada |
| Can., Bot. Soc. Ann. | Annals of the Botanical Society of Canada |
| Can. Chem. J. | The Canadian Chemical Journal |
| Can. Drug. | Canadian Druggist |
| Can. Eng. | Canadian Engineer, The |
| Can. Entom. | The Canadian Entomologist |
| Can. Entom. Soc. Rep. | First Annual Report on the Noxious Insects of the Province of Ontario |
| Can. Inst. Proc. | Proceedings of the Canadian Institute (Toronto, being a continuation of "The Canadian Journal of Science, Literature and History") |
| Can. Inst. Trans. | Transactions of the Canadian Institute |
| Can. J. | The Canadian Journal of Industry, Science, and Art |

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| Can. Naturalist | The Canadian Naturalist and Geologist, and Proceedings of the Natural History Society of Montreal |
| Can. P. | Canadian Patent |
| Can. Ppt. Off. Rec. | Canadian Patent Office Record |
| Can. Pharm. J. | Canadian Pharmaceutical Journal and Pharmaceutical Gazette |
| Can. Rec. Sci. | The Canadian Record of Science, including the Proceedings of the Natural History Society of Montreal, and replacing the Canadian Naturalist |
| Can. Roy. Soc. Proc. Trans. | Proceedings and Transactions of the Royal Society of Canada |
| Canestrini | See Archivio Zool. |
| Canestrini, Archiv. | Archivio per la Zoologia, l'Anatomia, e la Fisiologia |
| Cannes Soc. Mém. | Memoires de la Société des Sciences Naturelles (et Historiques), des Lettres et des Beaux-Arts de Cannes, et de l'arrondissement de Grasse |
| Cantu, Cronaca | Cronaca |
| Caout. Gutta-p. | Caoutchouc et la Gutta-percha |
| Caradoc Field Club Trans. | Transactions of the Caradoc and Severn Valley Field Club |
| Cardiff Natur. Soc. Trans. | Cardiff Naturalists' Society. Report and Transactions |
| Carinthia | See Kärnten |
| Carl, Rep. Physik. | Repertorium für Experimental-Physik., etc. (Rep. der Physik) |
| Carlsberg Lab. | See under Kiøbenh. |
| Karlsruhe | See Karlsruhe |
| Karlsruhe, Verh. Naturwiss. Ver. | Verhandlungen des Naturwissenschaftlichen Vereins |
| Carloinisches Medico-Chirurgisches Institut. | See under Stockh. Physiol. Lab. Mitth. |
| Carus, Zool. Anzeiger | Zoologischer Anzeiger |
| Casopis | Casopis pro Pestovani Matematiky a Fysiky. (Journal for the Advancement of Mathematics and Physica) |
| Casopis Cesketho Lekarn. | Casopis Cesketho Lekarnitura |
| Casper Vierteljahrssch. | Vierteljahrsschrift für gerichtliche und öffentliche Medicin |
| Casper Wochensch. | Wochenschrift für die gesammte Heilkunde |
| Cassel Jahr. | Jahresbericht, dann Bericht, über die Thätigkeit des Vereins für Naturkunde in Cassel |
| Cassier's Mag. | Cassiers's Magazine |
| Castings | Castings |
| Catania Atti Accad. Gioen. | Atti dell'Accademia Gioenia di Scienze Naturali di Catania |
| Catania Boll. Accad. Gioen. | Bollettino delle Sedute della Accademia Gioenia |
| Cattaneo Bibl. di Farm. | Biblioteca di Farmacia, Chimica, etc., |
| Cattaneo Giorn. Farm. | Giornale di Farmacia |
| Cell. Ind. | Die Celluloid Industrie |
| Cellule | La cellule |
| Cement | Cement |
| Cement Age | Cement Age |
| Cement Eng. News | Cement and Engineering News |
| Cement Record | Cement Record |
| Centr. Agrik. Chem. | Central-Blatt für Agrikulturchemie und rationellen Wirthschafts-Betrieb. Referirendes Organ für naturwissenschaftliche Forschungen in ihrer Anwendung auf die Landwirthschaft |
| Centr. Allg. Path. | Centralblatt für allgemeine Pathologie |

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| Centr. Bakt. | Centralblatt für Bacteriologie und Parasitenkunde |
| Centr. Med. Wiss. | Centralblatt für die medicinischen Wissenschaften |
| Centr. Mineral. | Centralblatt für Mineralogie, Geologie und Palaeontologie |
| Centr. Papierfabr. | Centralblatt für Papierfabrikation |
| Centr. Path. | Centralblatt für Allgemeine Pathologie und Pathologische Anatomie |
| Centr. Physiol. | Centralblatt für Physiologie |
| Centr. Text. Ind. | Centralblatt für die Textil-Industrie |
| Centr. Zuckerind. • | Centralblatt für die Zuckerindustrie |
| Centrztg. Optik. | Central-Zeitung für Optik und Mechanik (Elektrotechnik und verwandte Berufszweige) |
| Ceramique | Ceramique, La |
| Cette Stat. Maritime | See Montpellier Inst. Zool. Trav. |
| Cey. P. | Ceylon Patent |
| Chamb. Comm. J. | Chamber of Commerce Journal |
| Chambery Mem. Acad. Savoie. | Memoires de la Societe Academique de Savoie. |
| Charente-Inf. Soc. Sci. Ann. | Academie de la Rochelle. Societe des Sciences Naturelles de la Charente-Inférieure. Annales |
| Charkoff. | See Kharkov. |
| Charleston Med. Journ. | Charleston Medical Journal and Review |
| Charleston South J. Med. | The Southern Journal of Medicine |
| Chem. Age | Chemical Age |
| Chem. Centr. | Chemisches Centralblatt (1830-1906). |
| Chem. Coll. Reports | Reports of the Royal College of Chemistry, and Researches conducted in the Laboratories |
| Chem. Drug. | Chemist and Druggist, London |
| Chem. Drug. Australasia | Chemist and Druggist of Australasia |
| Chem. Eng. | Chemical Engineer |
| Chem. Gaz. | Chemical Gazette, The |
| Chem. Ind. | Chemische Industrie |
| Chem. Listy | Chemicke Listy |
| Chem. News | Chemical News |
| Chem. Pharm. Centr. Blatt. | Chemisch-pharmaceutisches Central-Blatt |
| Chem. Rev. | The Chemical Review |
| Chem. Rev. Fett-Harz-Ind. | Chemische Revue über die Fett-und Harz-Industrie |
| Chem. Tech. Mitth. | Elsner's Chemisch-Technische Mittheilungen |
| Chem. Tech. Rep. | Chemisch-Technisches Repertorium (Jacobsen 1862-1901) |
| Chem. Tech. Neuzeit | Chemische Technologie der Neuzeit |
| Chem. Tech. Übers. | Chemisch-Technische Übersicht (supplement to Chem. Ztg.) |
| Chem. Tech. Ztg. | Chemiker-und Techniker-Zeitung |
| Chem. Trade J. | Chemical Trade Journal and Chemical Engineer |
| Chem. Weekbl. | Chemisch Weekblad |
| Chem. World | Chemical World, The |
| Chem. Zentr. | Chemisches Zentralblatt (1907-) |
| Chem. Ztg. | Chemiker-Zeitung |
| Chem. Ztg. Rep. | Repertorium der Chemiker-Zeitung |
| Chem. Zts. | Chemische Zeitschrift |
| Chemist | The Chemist |
| Chemnitz Ber. | Bericht der Naturwissenschaftlichen Gesellschaft zu Chemnitz |
| Cherbourg, Mem. Soc. Acad. | Memoires de la Société Academique de Cherbourg |
| Cherbourg, Mem. Soc. Sci. | Memoires de la Société Imperiale des Science Naturelles de Cherbourg |

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| Cherbourg Soc. Sci. Natl. Mem. | Memoires de la Société Nationale des Sciences Naturelles et Mathématiques de Cherbourg |
| Chester Soc. Sci. Proc. | Proceedings of the Chester Society of Natural Science (and Literature) |
| Chicago Acad. Sci. Bull. | Bulletin of the Chicago Academy of Sciences |
| Chicago Acad. Sci. Bull. Nat. Hist. Surv. | The Chicago Academy of Sciences. Bulletin... of the Natural History Survey |
| Chicago Acad. Sci. Trans. | Transactions of the Chicago Academy of Sciences |
| Chicago Entom. Soc. Mem. | Occasional Memoirs of the Chicago Entomological Society |
| Chicago Field Columb. Mus. Publ. | Publications of the Field Columbian Museum |
| Chile, Anales Univ. | Anales de la Universidad de Chile |
| Chile P. | Chilean Patent |
| Chili Soc. Sci. Act. | Actes de la Société Scientifique du Chili (Actas de la Sociedad Científica de Chile) |
| Chim. et Ind. | Chimie et Industrie |
| Chimiste | Chimiste, Le |
| Christiania, Forh. | Forhandlinger i Videnskabs-Selskabet i Christiania |
| Christiania, Norsk Mag. | Norsk Magazin for Laegevidenskaben |
| Christiania Skr. (Math. Nat. Kl.) | Skrifter udgivne af Videnskabs-selskabet i Christiania. Matematisk-naturvidenskabelig Klasse |
| Christiania, Univers. Lab. | Das chemische Laboratorium der Universität Christiania |
| Chron. ind. | Chronique de l'industrie |
| Chur, Jahresber. Naturf. Gesell. | Jahresbericht der Naturforschenden Gesellschaft von Graubünden in Chur |
| Ciment | Ciment, Le |
| Cincin. Soc. Natur. Hist. J. | The Journal of the Cincinnati Society of Natural History |
| Cistula Entom. | Cistula Entomologica |
| Civil Eng. Inst. Trans. | Transactions of the Institution of Civil Engineers |
| Civil Eng. J. | The Civil Engineer and Architect's Journal, etc. |
| Civilingenieur | Der Civilingenieur |
| Clay Worker | Clay Worker, The |
| Clermont, Mem. Acad. Sci. | Memoires de l'Academie des Sciences, Belles Lettres, Arts de Clermont-Ferrand |
| Cleveland Med. J. | Cleveland Medical Journal |
| Clin. Soc. Trans. | Transactions of the Clinical Society of London |
| Coblentz, Jahr. bot. Ver. | Jahresbericht des botanischen Vereines am Mitten und Niederrheine, mit botanischen Abhandlungen |
| Cohn, Beitr. Biol. Pflanz. | Beiträge zur Biologie der Pflanzen |
| Coimbra, Inst. | O Instituto, journal scientifico et letterario |
| Coimbra, Soc. Bróter. Bol. | Sociedade Broteriana. Boletim Anual |
| Col. P. | Colombian Patent |
| Collegium | Collegium (Scientific technical supplement to Ledermarkt) |
| Colliery Guardian | Colliery Guardian and Journal of the Iron and Coal Trades |
| Colmar Soc. Hist. Natur. Bull. | Bulletin de la Société d'Histoire Naturelle de Colmar |
| Colombia, Contrib. | Contribuciones de Colombia a las Ciencias i a las Artes |
| Colombo | See Ceylon |
| Colorado Sci. Soc. Proc. | Proceedings of the Colorado Scientific Society |
| Comment. Fauna &c. Ven. Trent. | Commentario della Fauna, Flora e Gea del Veneto e Trentino |
| Compt. rend. | Comptes rendus hebdomadaires des Seances de l'Academie des Sciences |

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| Compt. rend. Assoc. Franc. | Association Francaise pour l'Avancement des Sciences. Compte Rendu de la 1 ^e (-12 ^e) Session; 1872-83 |
| Compt. rend. minerale | Comptes rendus de la Société de l'industrie minerale |
| Compt. rend. Soc. biol. | Comptes rendus des seances et memoires de la Société de biologie, Paris |
| Compt. rend. trav. lab. Carlsberg | Comptes rendus du travaux du laboratoire de Carls- berg |
| Concrete | Concrete |
| Concrete Age | Concrete Age |
| Concrete Constr. Eng. | Concrete and Constructional Engineering |
| Concrete Eng. | Concrete Engineering (no longer published separately. Combined with Cement Age) |
| Conegliano Scuola Vit. Enol. Ann. | Annali della R. Scuola di Viticoltura e di Enologia in Conegliano |
| Conegliano Scuola Vit. Enol. N. Rassegna | Nuova Rassegna di Viticoltura de Enologia della R. Scuola di Conegliano |
| Conegliano Scuola Vit. Enol. Riv. | La Rivista. Periodico (quindicinale, Organo) della R. Scuola di Viticoltura e di Enologia (e del Comizio Agrario) di Conegliano |
| Cong. P. | Congo Free State Patent |
| Congr. Anthropol. Compt. Rend. | Congres international d'Anthropologie et d'Archeologie prehistoriques. Comptes Rendus |
| Congr. Bot. Crittog. Atti | Societa Crittogamologica Italiana. Atti del Congresso Nazionale di Botanica Crittogamica in Parma |
| Congr. Bot. Int. Atti | Atti del Congresso Internazionale di Genova |
| Congr. Int. Bot. Bull. | Bulletin du Congres International de Botanique et d'Horticulture reuni a St. Petersburg... |
| Congr. Internatl. Hortic. Bull. | Bulletin du Congres International d'Horticulture a Bruxelles |
| Congr. Internatl. Med. Atti | Atti dell' XI. Congresso Medico Internazionale |
| Congr. Internatl. Med. C. R. | Comptes Rendus du XII Congres International de Medecine |
| Congr. Internatl. Sci. Med. C. R. | Congres Periodique International des Sciences Medi- cales. Compte-Rendu |
| Congr. Internatl. Zool. (C. R.) | Congres International de Zoologie |
| Connecticut, Acad. Mem. | Memoirs of the Connecticut Academy of Arts and Sciences |
| Connecticut Acad. Trans. | Transactions of the Connecticut Academy of Arts and Sciences |
| Contrib. Biol. Veg. | Contribuzioni alla Biologia Vegetale |
| Copenhagen | See Kjobenhavn. |
| Copenhagen | See Congr. Int. Sci. Med. C. R., 1884 |
| Copenhagen, Résumé | Résumé du Bulletin de la Société Royale Danoise des Sciences |
| Cordoba, Acad. Bol. | Boletin de la Academia Nacional de Ciencias Exactas existente en la Universidad de Cordoba |
| Cordoba Acad. Ci. Act. | Actas de la Academia Nacional de Ciencias en Cordoba |
| Corn Trade J. | Corn Trade Journal |
| Cornwall, J. Roy. Inst. | Journal of the Royal Institution of Cornwall |
| Cornwall Poly. Soc. Rep. | Royal Cornwall Polytechnic Society, Annual Report |
| Cornwall, Poly. Soc. Trans. | Reports and Transactions of the Royal Geological Society of Cornwall |
| Corresp. Blatt. Schweiz. Aerzte | Correspondenz-Blatt für Schweizer Aerzte |
| Corresp. Blatt Zahn. | Correspondenzblatt für Zahnärzte |
| Cosmos | Cosmos: Revue Encyclopedique hebdomadaire |

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| Costa, Corrisp. Zool. | Corrispondenza Zoologica, destinata a diffondere nel regno delle Due Sicilie tutto cio che si va discoprendo entro e fuori Europa (e vice-versa), risguardante la Zoologia in generale |
| Cotteswold Club Proc. | Proceedings of the Cotteswold Naturalists' Field Club |
| Cracovie Acad. Sci. Bull | Bulletin International de l'Academie des Sciences de Cracovie |
| Cracow | See Krakow |
| Crell. Ann. | Chemische Annalen für die Freunde der Naturlehre, etc. |
| Crichton, Russ. Sammlung. | Russische Sammlung für Naturwissenschaft und Heilkunst |
| Cron. med. mex. | Cronica medica mexicana, Mexico |
| Croydon Micro. Club Proc. | Proceedings and Transactions of the Croydon Microscopical and Natural History Club |
| Croydon Micro. Club Rep. | Report and Abstract of Proceedings of the Croydon Microscopical (and Natural History) Club |
| Cuba P. | Cuban Patent |
| Cuba, Rep. Fis. Nat. | Repertorio fisico-naturale de la isla de Cuba |
| Cuir | Cuir, Le |
| Cumberland, Assoc. Trans. | Transactions of the Cumberland and Westmorland Association for the Advancement of Literature and Science |
| Cuyper, Rev. Univ. | Revue Universelle des Mines, de la Metallurgie, &c. |
| D'Alton u. Burm. Ztg. Zool. | Zeitung für Zoologie, Zootomie, und Palaeozoologie |
| Dan. Biol. Stat. Rep. | Report of the Danish Biological Station to the Home Department (Board of Agriculture) |
| Dan. P. | Danish Patent |
| Danzig, Neu. Schrift. | Neueste Schriften der Naturforschenden Gesellschaft in Danzig |
| Danzig, Schrift. | Schriften der Naturforschenden Gesellschaft in Danzig |
| Darmst. Beitr. Geol. | Beiträge zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden |
| Darmst. Ver. Erdk. Notiz. | Notizblatt des Vereins für Erdkunde zu Darmstadt und des Mittelrheinischen Geologischen Vereins |
| Davenport Acad. Proc. | Proceedings of the Davenport Academy of Natural Sciences |
| Dax Soc. Borda Bull. | (Bulletin de la) Société de Borda, Dax (Landes) |
| Delft Ecole Poly. Ann. | Annales de l'Ecole Polytechnique de Delft |
| Delhi, Med. J. | Quarterly Medical and Surgical Journal for the North-West Provinces |
| Denison Univ. Sci. Lab. Bull. | Bulletin of (the Scientific Laboratories of) Denison University |
| Dent. Cosmos | Dental Cosmos, Philadelphia |
| Dent. Digest | The Dental Digest, Chicago |
| Dent. Rev. | The Dental Review |
| Deut. Amer. Apoth. Ztg. | Deutsch-Amerikanische Apotheker Zeitung, New York |
| Deut. Amer. Gewerbeztg. | Illustrierte Deutsch-Amerikanische Gewerbe und Industrie-Zeitung (Newark, N. J.) |
| Deut. Arch. Klin. Med. | Deutsches Archiv. für Klinische Medizin |
| Deut. Bot. Ges. Ber. | Berichte der Deutschen Botanischen Gesellschaft |
| Deut. Bot. Monats. | Deutsche Botanische Monatsschrift |
| Deut. Buchdr. Ztg. | Deutsche Buchdrucker-Zeitung |
| Deut. Eisenbahn Ztg. | Zeitung des Vereins Deutscher Eisenbahn-Verwaltungen |
| Deut. Elektro. Ges. | See Zts. Elektroch. |

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| Deut. Entom. Zts. | Deutsche Entomologische Zeitschrift (formerly <i>Berliner Entomologische Zeitschrift</i>) |
| Deut. Geol. Ges. Zts. | Zeitschrift der Deutschen Geologischen Gesellschaft |
| Deut. Gerber Ztg. | Deutsche Gerber Zeitung |
| Deut. Ind. Ztg. | Deutsche Industrie Zeitung |
| Deut. Klinik | Deutsche Klinik |
| Deut. Mechan. Ztg. | Deutsche Mechaniker-Zeitung |
| Deut. med. Wochenschr. | Deutsche medizinische Wochenschrift |
| Deut. Monats. | Deutsche Monatshefte |
| Deut. Naturf. Ber. | Amtlicher Bericht der... Versammlung Deutscher Naturforscher und Aerzte |
| Deut. Naturf. Festschr. | Festschrift für die... Versammlung Deutscher Naturforscher und Aerzte |
| Deut. Naturf. Tagebl. | Tageblatt der Versammlung Deutscher Naturforscher und Aerzte |
| Deut. Naturf. Versamml. Ber. | Bericht über die Versammlung der Deutschen Naturforscher und Aerzte |
| Deut. Poly. Ztg. | Allgemeine Deutsche Polytechnische Zeitung (H. Grothe) |
| Deut. Phys. Ges. Verh. | Verhandlungen der Deutschen Physikalischen Gesellschaft... |
| Deut. Tech. Ztg. | Deutsche Techniker Zeitung |
| Deut. Töpfer Ziegl. Ztg. | Deutsche Töpfer und Ziegler Zeitung |
| Deut. Vierteljahrshr. Oeff. Gesundh. | Deutsche Vierteljahrsschrift für Gesundheitspflege |
| Deut. Zool. Ges. | See Zool. Anz. |
| Deut. Zool. Ges. Verh. | Verhandlungen der Deutschen Zoologischen Gesellschaft |
| Deut. Zts. Chirurg. | Deutsche Zeitschrift für Chirurgie |
| Deut. Zts. Thiermed. | Deutsche Zeitschrift für Thiermedizin und vergleichende Pathologie |
| Deut. Zuckerind. | Deutsche Zuckerindustrie |
| Devon. Assoc. Trans. | Transactions of the Devonshire Association for the Advancement of Science, Literature and Art |
| Devon & Cornwall Natur. Hist. Soc. | See Plymouth Inst. Trans. |
| Diamant Ztg. | Diamant, Glas-Industrie Zeitung |
| Dietet. Hyg. Gaz. | Dietetic and Hygienic Gazette, The |
| Dijon, Acad. Sci. Mem. | Memoires de l'Academie des Sciences, Arts et Belles-Lettres de Dijon |
| Dijon, J. Agric. | Journal d'Agriculture de la Cote d'Or. |
| Dijon, Seances Acad. | Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Dijon |
| Dinant, Soc. Natur. Bull. | Bulletin de la Société des Naturalistes Dinantais |
| Dingl. Poly. | Dinglers Polytechnisches Journal |
| Donders, Archiv | Archiv für die Holländischen Beiträge zur Natur- und Heilkunde |
| Dorpat, Archiv | Archiv für die Naturkunde Liv-, Esth-, und Kurlands |
| Dorpat, Biol. Naturk. | Biologische Naturkind. |
| Dorpat, Naturf. Ges. | See Arch. Nat. (Dorpat) |
| Dorpat, Naturwiss. Abh. | Naturwissenschaftliche Abhandlungen aus Dorpat |
| Dorpat Pharm. Inst. Arb. | Arbeiten des Pharmakologischen Institutes zu Dorpat |
| Dorpat Sitzber. | Sitzungsberichte der Naturforscher-Gesellschaft bei der Universität (Jurjew) Dorpat |
| Dorpat Schr. | Schriften herausgegeben von der Naturforscher Gesellschaft bei der Universität (Jurjew) Dorpat |
| Dorset Field Club Proc. | Proceedings of the Dorset Natural History and Antiquarian Field Club |

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| Douai Mem. Soc. Agric. | Memoires de la Société d'Agriculture, de Sciences, et d'Arts, seant a Douai |
| Doubs Soc. Emul. Mem. | Memoires de la Société d'Emulation du Departement du Doubs |
| Dove Rep. Physik. | Repertorium der Physik. Enthaltend eine vollständige Zusammenstellung der neuern Fortschritte dieser Wissenschaft |
| Dresden Ausz. Protokoll. | Auszüge aus den Protokollen der Gesellschaft für Natur- und Heilkunde in Dresden |
| Dresden Denkschr. Naturwiss. Ges. Isis. | Denkschriften der Naturwissenschaftlichen Gesellschaft Isis zu Dresden |
| Dresden Entom. Ver. "Iris" Corresp.-Bl. | See Iris |
| Dresden Isis Festschr. | Festschrift der Naturwissenschaftlichen Gesellschaft Isis in Dresden |
| Dresden Isis Sitzber. | Sitzungsberichte und Abhandlungen der Naturwissenschaftlichen Gesellschaft Isis in Dresden |
| Dresden, Jahr. Natur. Heilk. | Jahresberichte für 1858-60 v. d. Gesellschaft für Natur- und Heilkunde in Dresden |
| Dresden, Mitth. Poly. Schule | Mittheilungen der K. Sächs. Polytechnischen Schule |
| Dresden, Schr. Ges. Mineral. | Auswahl aus den Schriften der unter Werner's Mitwirkung gestifteten Gesellschaft für Mineralogie |
| Dresden, Sitzber. Natur. Heilk. | Sitzungsberichte der Gesellschaft für Natur- und Heilkunde |
| D. R. P. | German Patent (Deutsches Reichs-Patent) |
| Drug. Circ. | Druggist's Circular |
| Drug Topics | Drug Topics, New York |
| Dublin, Geol. Soc. J. | Journal of the Geological Society of Dublin |
| Dublin, Hosp. Gaz. | Dublin Hospital Gazette |
| Dublin J. Med. Chem. Sci. | Dublin Journal of Medical and Chemical Science |
| Dublin J. Med. Sci. | The Dublin Journal of Medical Science |
| Dublin Med. Trans. | Dublin Medical Transactions |
| Dublin Micro. Club | See Irish Natur. |
| Dublin, Natur. Hist. Soc. Proc. | Proceedings of the Natural History Society of Dublin |
| Dublin Natur. Field Club | See Irish Natur. |
| Dublin, Pathol. Soc. Proc. | Proceedings of the Pathological Society of Dublin |
| Dublin Quart. J. | The Dublin Quarterly Journal of Science |
| Dublin Quart. J. Med. | Dublin Quarterly Journal of Medical Science |
| Dublin, Roy. Soc. J. | Journal of the Royal Dublin Society |
| Dublin Soc. J., Dublin Soc. Trans. | Transactions and Journal of the Dublin Society |
| Dublin Soc. Sci. Proc. | The Scientific Proceedings of the Royal Dublin Society |
| Dublin Soc. Sci. Trans. | The Scientific Transactions of the Royal Dublin Society |
| Dublin, Zool. Bot. Assoc. Proc. | Proceedings of the Dublin University Zoological and Botanical Association |
| Dudley, Geol. Soc. Proc. | Transactions of the Dudley and Midland Geological and Scientific Society |
| Dumfr. Gallow. Soc. Trans. | The Transactions and Journal of Proceedings of the Dumfriesshire and Galloway Natural History and Antiquarian Society |
| Dunkerque, Mem. Soc. Encour. | Memoires de la Société Dunkerquoise pour l'Encouragement des Sciences, des Lettres, et des Arts |
| Durham Univ. Phil. Soc. Proc. | Proceedings of the University of Durham Philosophical Society |

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| Dyer, Calico Ptr. | Dyer, Calico Printer, Bleacher, Finisher, and Textile Review |
| Dzondi, Aeskulap | Aeskulap |
| Eastbourne Natur. Hist. Soc. Papers (& Trans.) | Papers (Transactions) of the Eastbourne Natural History Society |
| Eastbourne Natur. Hist. Soc. Proc. | The Sixth Annual Report of the Eastbourne Natural History Society |
| Eastbourne Natur. Hist. Soc. Trans. | Transactions of the Eastbourne Natural History Society |
| Echange | L'Echange. Organe (Mensuel) des Naturalistes de la Region Lyonnaise |
| Eckhard, Beitr. | Beiträge zur Anatomie und Physiologie |
| Eclairage Elect. | L'Eclairage Electrique. Revue (hebdomadaire) d'(el) Electricite |
| Eclat. Med. J., Cincin. | Eclectic Medical Journal, Cincinnati |
| Econ. Geol. | Economic Geology |
| Ecu. P. | Ecuador Patent |
| Edinb. Bot. Soc. Proc. | Proceedings of the Botanical Society of Edinburgh for the years 1855-56 |
| Edinb. Bot. Soc. Trans. | Transactions of the Botanical Society of Edinburgh |
| Edinb. Field Club Trans. | Transactions of the Edinburgh Naturalists' Field Club |
| Edinb., Fish. Bd. Rep. | Annual Report of the Fishery Board for Scotland |
| Edinb. J. Med. Sci. | Edinburgh Journal of Medical Science |
| Edinb. J. Natur. Geogr. Sci. | The Edinburgh Journal of Natural and Geographical Science |
| Edinb. J. Sci. | The Edinburgh Journal of Science |
| Edinb. Med. Chir. Soc. Trans. | Transactions of the Medico-Chirurgical Society of Edinburgh |
| Edin. Med. J. | Edinburgh Medical Journal |
| Edinb. Mem. Wern. Soc. | Memoirs of the Wernerian Natural History Society |
| Edinb. Monthly J. Med. Sci. | Edinburgh Monthly Journal of Medical Science |
| Edinb. Natur. Soc. Trans. | Transactions of the Edinburgh Field Naturalists' and Microscopical Society, instituted as the Edinburgh Naturalists' Field Club |
| Edinb. N. Phil. J. | The Edinburgh New Philosophical Journal |
| Edinb. Phil. J. | The Edinburgh Philosophical Journal |
| Edinb. Plin. Soc. Trans. | Transactions of the Plinian Society |
| Edinb. Proc. Phys. Soc. | Proceedings of the Royal Physical Society of Edinburgh |
| Edinb. Roy. Coll. Physns. Lab. Rep. | Reports from the Laboratory of the Royal College of Physicians, Edinburgh |
| Edinb. Roy. Soc. Proc. | Proceedings of the Royal Society of Edinburgh |
| Edinb. Roy. Soc. Trans. | Transactions of the Royal Society of Edinburgh |
| Edinb. Trans. Scot. Soc. Arts | Transactions of the Royal Scottish Society of Arts |
| Eisen Ztg. | Eisen Zeitung |
| Ekaterinburg | See Iekaterinenb. |
| Elberfeld Naturwiss. Ver. Jahrb. | Jahres-Bericht des Naturwissenschaftlichen Vereins in Elberfeld |
| Elec. Rev. | The Electrical Review |
| Elec. Soc. Trans. | The Transactions and Proceedings of the London Electrical Society |
| Elec. Telegr. Rev. | The Electric Telegraph Review |
| Elec. World | Electrical World |
| Electrician | The Electrician |
| Electricite | L'Electricite |
| Electrochem. Met. Ind. | Electrochemical and Metallurgical Industry |

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| Elektrochem. Zts. | Elektrochemische Zeitschrift. |
| Elektrotech. Zts. | Electrotechnische Zeitschrift |
| Elliott Soc. J. | Journal of the Elliott Society of Natural History |
| Elliott Soc. Proc. | Proceedings of the Elliott Society of Natural History |
| Elsner, Mitth. | See Chem. Tech. Mitth. |
| Emden Naturf. Ges. Jahr. | ... Jahresbericht der Naturforschenden Gesellschaft in Emden |
| Emden Naturf. Ges. Schr. | Kleine Schriften der Naturforschenden Gesellschaft in Emden |
| Eng. | Engineering |
| Eng. Contr. | Engineering and Contracting |
| Eng. Digest | Engineering Digest |
| Eng. Mag. | Engineering Magazine, The |
| Eng. Mining J. (Eng. Min. J.) | Engineering and Mining Journal, The |
| Eng. News | Engineering News |
| Eng. Record | Engineering Record, Building Record and Sanitary Engineer |
| Engineer | Engineer, The |
| Engineers' J. | The Engineers' Journal and Railway Gazette of India and the Colonies |
| Engineers Soc. Trans. | Society of Engineers. Transactions |
| Engl. Mech. | English Mechanic |
| Engler, Bot. Jahr. | Botanische Jahrbücher für Systematik, Pflanzengeschichte und Pflanzengeographie |
| Engrais, L' | Engrais, L' |
| Entom. Annual | The Entomologist's Annual |
| Entom. Mag. | The Entomological Magazine |
| Entom. Medd. (Kjobenh.) | Entomologiske Meddelelser udgivne af Entomologisk Forening |
| Entom. Month. Mag. | The Entomologist's Monthly Magazine |
| Entom. Nachr. | Entomologische Nachrichten |
| Entom. Record | The Entomologist's Record and Journal of Variation |
| Entom. Soc. Trans. | The Transactions of the Entomological Society of London |
| Entom. Tidskr. | Entomologisk Tidskrift på Föranstaltande af Entomologiska Foreningen i Stockholm |
| Entomologica Amer. | Entomologica Americana |
| Entomologist | The Entomologist |
| E. P. | English (British) Patent |
| Epicure | Epicure, The |
| Epidem. Soc. Trans. | Transactions of the Epidemiological Society of London |
| Epinal (Vosges) Ann. | Annales de la Société d'Emulation du departement des Vosges |
| Erdel. Muz. Etyl. Értek. | Az Erdelyi Múzeum-Egyet. Kiadványai Értekezések. (Publications of the Transylvanian Museum Association. Memoirs) |
| Erdmann, Sveriges Geol. Undersök. | Sveriges geologiska Undersökning, på offentlig bekostnad, utförd under Ledning af A. Erdmann. |
| Erfurt, Abh. Akad. Wiss. | Abhandlungen der Kurfürstlich Mainzer Akademie nützlicher Wissenschaften zu Erfurt |
| Erfurt, Akad. Jahr. | Jahrbücher der königlichen Akademie gemeinnütziger Wissenschaften zu Erfurt |
| Erfurt, Denkschr. | Denkschrift der Akademie gemeinnütziger Wissenschaften in Erfurt |
| Erfurt, Nova Acta | Nova Acta Academiae Electoralis Moguntinae Scientiarum utilium quae Erfurti est. |

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| Ergeb. Physiol. | Ergoebnisse der Physiologie, Wiesbaden |
| Erlangen, Abb. | Abhandlungen der Physikalisch-medicinischen Societät in Erlangen |
| Erlangen Anat. Inst. | See Beitr. Morphol. |
| Erlangen, Mitth. Phys. Med. Soc. | Wissenschaftliche Mittheilungen der Physikalisch-medicinischen Societät zu Erlangen |
| Erlangen Phys. Med. Soc. Sitzber. | Sitzungsberichte der Physikalisch-Medizinischen Societät zu (in) Erlangen |
| Erythea | Erythea. A Journal of Botany, West American and General |
| Essex Field Club Proc. | Journal of Proceedings of the Essex Field Club |
| Essex Field Club Spec. Mem. | Essex Field Club Special Memoirs |
| Essex Field Club Trans. | Transactions of the Essex Field Club |
| Essex Inst. Bull. | Bulletin of the Essex Institute |
| Essex Inst. Commun. | Communications read before the Essex Institute |
| Essex Inst. Proc. | Proceedings of the Essex Institute |
| Essex Natur. Hist. Soc. J. | Journal of the Essex County Natural History Society |
| Essex Natlist. | The Essex Naturalist |
| Essig, Ind. | Deutsche Essigindustrie |
| Etudes Gites Mineraux | See France Gites Min. Etudes |
| Eure, Bull. Acad. Ebroic. | Bulletin de l'Academie Ebroicenne |
| Eure, J. Agric. | Journal d'Agriculture, de Medicine et des Sciences accessoires |
| Eure, Recueil Trav. | Recueil des Travaux de la Société Libre d'Agriculture, des Sciences, des Arts et des Belles-Lettres du departement de l'Eure |
| Eure, Soc. Agric. Bull. | Bulletin de la Société d'Agriculture, des Sciences, et des Arts du departement de l'Eure |
| Eure, Soc. Agric. Recueil | Recueil de la Société d'Agriculture, Sciences, Arts, et Belles-Lettres du departement de l'Eurs |
| Evkönyv | A' Magyar Tudos Tarsasag' Evkönyvei |
| Exner, Rep. | Repertorium der Physik. |
| Exper. Sta. Rec. | Experiment Station Record |
| Eyr | Eyr, et Medicinisk Tidsskrift |
| Fachgenosse | Fachgenosse, Der |
| Falaise, Mem. Soc. Acad. | Memoires de la Société Academique des Sciences, &c., de Falaise |
| Farben Ztg. | Farben Zeitung |
| Färb. Ztg. | Färber Zeitung (Lehne's) |
| Fechner Centr. | Centralblatt für Naturwissenschaften und Anthropologie |
| Fechner, Rep. | Repertorium der Experimental-Physik. |
| Fed. Inst. Min. Engin. Trans. | Transactions of the Federated Institution of Mining Engineers |
| Fer. | Ferrum, Halle |
| Ferussac, Bull. Sci. Math. | Bulletin des Sciences Mathematiques, Astronomiques, Physiques, et Chimiques par le Baron de Ferussac |
| Ferussac, Bull. Sci. Natur. | Bulletin des Sciences Naturelles et de Geologie |
| Feuille Jeunes Natur. | Feuille des Jeunes Naturalistes |
| Field Mus. Natur. Hist. | Field Museum of Natural History, Chicago, Publication |
| Fij. P. | Fiji Islands Patent |
| Fin. P. | Finland Patent |
| Finistere Soc. Sci. Bull. | Bulletin de la Société d'Etudes Scientifiques du Finistere |
| Finlande Soc. Geogr. | See Fennia |
| Finska Läk. Sällsk. Handl. | Finska Läkare Sällskapets Handlingar |
| Finska Vet.-Soc. | See Helsingfors, Bidrag. Helsingfors, Öfvers |

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| Firenze Accad. Georgofili Atti | Atti della Reale Accademia Economico-Agraria dei Georgofili di Firenze |
| Firenze, Ann. Mus. Fis. | Annali del R. Museo di Fisica e Storia Naturale |
| Firenze, Ann. Mus. Imp. | Annali del Museo Imperiale di Fisica e Storia Naturale di Firenze |
| Firenze Congr. Bot. Atti | Atti del Congresso Internazionale Botanico tenuto in Firenze nel mese di Maggio 1874 |
| Firenze, Mem. Soc. Ital. | ^a See Modena |
| Firenze, Opusc. Sci. | Collezione d'Opuscoli scientifici. |
| Firenze R. Inst. Pubbl. | Pubblicazioni del R. Istituto di Studi Superiori Pratiche di Perfezionamento in Firenze |
| Firenze Soc. Georgofili Atti | Atti della (Real) Società Economica di Firenze ossia de' Georgofili |
| Firenze Soc. Studi Geogr. Boll. | See Riv. Geogr. Ital. |
| Flora | ^f Flora oder Allgemeine Botanische Zeitung |
| Flore Jardins | Annales d'Horticulture et de Botanique, ou Flore des Jardins du Royaume des Pays-Bas |
| Flore Serres | Flore des Serres et des Jardins de l'Europe |
| Florence | See Firenze |
| Flörke, Repert. | Repertorium des neuesten und wissenwürdigsten aus der gesammten Naturkunde |
| Földt. Közlön | Földtani Közlöny, Havi folyóirat kiadja a Magyarhoni Földtani Tarsulat |
| Folia Clin. | Folia clinica chimico et microscopica |
| Folia haematol. | Folia haematologica |
| Folia Therap. Lond. | Folia Therapeutica, London |
| Forbes, Med. Rev. | The British and Foreign Medical Review, or Quarterly Journal of Practical Medicine and Surgery |
| Forsch. Agr.-Phys. | Forschungen auf dem Gebiete der Agrikultur-Physik. |
| Förster, Allg. Bauztg. | Allgemeine Bauzeitung |
| Fortschr. Chem. | Fortschritte der Chemie, Physik und Physikalischen chemie |
| Fortschr. Med. | Fortschritte der Medicin. |
| Fortschr. Phys. | Die Fortschritte der Physik. |
| Fortschr. Röntgenstr. | Fortschritte auf dem Gebiete der Röntgenstrahlen |
| Fortschr. Theerfarben-Fabrikation | Fortschritte der Theerfarbenfabrikation und verwandter Industriezweige |
| Foundry | Foundry, The |
| F. P. | French Patent |
| France, Congr. Med. Chir. | Congres Medico-Chirurgicale de France |
| France, Congr. Sci. | Sessions des Congres Scientifiques de France |
| France Gites Miner. Etudes | Etudes des Gites Mineraux de la France |
| France, Inst. Provinces Annuaire | Annuaire de l'Institut des Provinces et des Congres Scientifiques de France |
| France, Inst. Provinces Mem. | Memoires de l'Institut des Provinces de France: Sciences physiques et naturelles |
| France Soc. Agric. Bull. | Bulletin des Seances de la Société Nationale d'Agriculture de France |
| France Soc. Agric. Mem. | Memoires publies par la Société Nationale d'Agriculture de France |
| France Soc. Bot. Bull. | Bulletin de la Société Botanique de France |
| France Soc. Entom. | See Abeille., Paris, Soc. Ent. Ann., Paris, Soc. Ent. Bull., Rev. Ent. |
| Franc Soc. Miner. Bull. | Bulletin de la Société Mineralogique de France. Bulletin de la Société Francaise de Mineralogie. (Ancienne Société Mineralogique de France) |
| France Soc. Zool. | See Paris, Caus. Sci. |
| France Soc. Zool. Bull. | Bulletin de la Société Zoologique de France |

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| France Soc. Zool. Mem. | Memoires de la Société Zoologique de France |
| Frankfurt | See Senckenberg |
| Frankfurt, Jahr. Phys. Ver. | Jahrbuch zur Verbreitung naturwissenschaftlicher Kenntnisse, veranstaltet vom Physikalischen Verein zu Frankfurt a/Main |
| Frankf. Ver. Pflege Phot. | See Wien, Photogr. Correspond. |
| Frankfurt, Zool. Garten | Der Zoologische Garten Frankfurt a/M. |
| Frankfurter Zts. Pathol. | Frankfurter Zeitschrift für Pathologie |
| Französ. Ann. | Französische Annalen für die allgemeine Naturgeschichte, Physik, &c. |
| Freiberg, Jahr. Berg. Hütt. | Jahrbuch für den Berg- und Hüttenmann. Herausg. von der Königl. Berg-Akademie zu Freiberg |
| Freiburg, Beitr. | Beiträge zur Rheinischen Naturgeschichte. |
| Freiburg, Ber. | Berichte über die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B. |
| Freie K. | Freie Künste |
| Frelon | Le Frelon. Journal d'Entomologie descriptive |
| Fries, Bot. Notiser | Botaniska Notiser |
| Froriep, Notizen | Notizen aus dem Gebiete der Natur- und Heilkunde |
| Pfuhling's Ztg. | Pfuhling's landwirtschaftliche Zeitung |
| Gac. ind. | La Gaceta industrial |
| Gand, Ann. Soc. Agric. | Annales de la Société Royale d'Agriculture et de Botanique |
| Gand, Ann. Soc. Med. | Annales de la Société de Medecine de Gand |
| Gand, Bull. Soc. Med. | Bulletin de la Société de Medecine de Gand |
| Gard, Aperçu Trav. | Notice ou Aperçu analytique des Travaux de l'Academie Royale du Gard |
| Gard, Mem. Acad. | Memoires de l'Academie du Gard |
| Gard, Notice Trav. Acad. | Notice des Travaux de l'Academie du Gard |
| Garden & Forest | Garden and Forest. A Journal of Horticulture, Landscape Art and Forestry |
| Gardeners Chron. | The Gardeners Chronicle |
| Garnett, Ann. Phil. | Annals of Philosophy, Natural History, Chemistry &c. |
| Garten-Flora | Garten-Flora |
| Garten-Ztg. | Neue allgemeine Deutsche Garten- und Blumenzeitung |
| Gartenwelt | Gartenwelt, The |
| Gas World | Gas World, The |
| Gaz | Le Gaz |
| Gazz. del. Clin. | Gazzetta della Cliniche |
| Gazz. med. ital lomb. | Gazzetta medica italiana lombardia, Milano |
| Gazz. Chim. Ital. | Gazzetta Chimica Italiana |
| Geelong Field Natur. Club | See Wombat |
| Gehlen J. | Journal für die Chemie und Physik |
| Gendrin, Trans. Med. | Transactions Medicales |
| Geneeskundig Mag. | Geneeskundig Magazijn |
| Geneve, Archiv. | See Archives Sci. Phys. Nat. |
| Geneve, Bull. Soc. Ornith Suisse. | Bulletin de la Société Ornithologique Suisse |
| Geneve Conserv. Bot. Annuaire | Annuaire du Conservatoire du Jardin Botanique de Geneve |
| Geneve, Inst. Natl. Bull. | Bulletin de l'Institut National Genevois |
| Geneve, Inst. Natl. Mem. | Memoires de l'Institut National Genevois |
| Geneve, Mus. Hist. Natur. Ann. | See Rev. Suisse Zool. |
| Geneve, Recueil Trav. Soc. Med. | Recueil des Travaux de la Société Medicale de Geneve |
| Geneve, Soc. Geogr. Mem. | Memoires de la Société de Geographie de Geneve |

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| Geneve, Soc. Phys. Mem. | Memoires de la Société de Physique et d'Histoire Naturelle de Geneve |
| Genie civ. | Genie Civil |
| Genova | See Congr. Bot. Int. Atti. 1892 |
| Genova, Ann. Mus. Phys. | Annali del Museo Civico di Storia Naturale |
| Genova, Giorn. | Giornale degli Studiosi di Lettere, Scienze, arti e Mestieri |
| Genova, Mem. Accad. | Memoire dell'Accademia Imperiale delle Scienze di Genova |
| Genova, Mem. Ist. Ligure. | Memorie dell' Istituto Ligure |
| Genova, Mem. Soc. Med. Emul. | Memorie della Società Medica di Emulazione di Genova |
| Genova Mus. Civ. Ann. | Annali del Museo Civico di Storia Naturale di Genova |
| Genova Mus. Zool. Anat. Comp. Boll. | Bollettino dei Musei di Zoologia e Anatomia Comparata della R. Università di Genova |
| Genova, Soc. Ligust. Atti | Atti della Società Ligustica di Scienze Naturali e Geografiche |
| Genova Univ. Atti | Atti della R. Università di Genova |
| Geogr. Soc. J. | Journal of the Royal Geographical Society of London |
| Geogr. Soc. Proc. | Proceedings of the Royal Geographical Society and Monthly Record of Geography |
| Geogr. Soc. Suppl. Pap. | Royal Geographical Society. Supplementary Papers |
| Geol. Mag. | Geological Magazine |
| Geol. Survey, Can. | Geological Survey, Canada |
| Gera, Naturwiss. Jahr. | Jahresbericht der Gesellschaft von Freunden der Naturwissenschaften in Gera, nebst Nachrichten über den Naturwissenschaftlichen Verein in Schleiz |
| Gerber | Der Gerber |
| Germar, Mag. Entom. | Magazin der Entomologie |
| Germar, Zts. Entom. | Zeitschrift für die Entomologie |
| Gergonne, Ann. Math. | Annales de Mathématique |
| Gesundh. Ing. | Gesundheits-Ingenieur |
| Gew. Ztg. | Wick's Gewerbezeitung |
| Gewerbebl. Schw. | Schweizerisches Gewerbeblatt |
| Gewerbebl. Würt | Gewerbeblatt aus Württemberg |
| Gewerbebl. | Gewerbehalle |
| Gewerks Ztg. | Oesterreichische Gewerkszeitung |
| Giessen, Oberhess. Ges. Ber. | Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde |
| Gievel, Zts. | See Zts. Gesamt. Naturwiss. |
| Gilbert, Ann. Phys. | See Ann. Phys. |
| Gill, Tech. Micro. Repos. | Technical and Microscopical Repository |
| Giorn. Arcad. | Giornale Arcadico di Scienze |
| Giorn. farm. chim. | Giornale de farmacia, di chimica |
| Giorn. Gen. civ. | Giornale del Genio civile |
| Giron. Ist. Lomb. | See Bibl. Ital. |
| Giorn. Mineral. Crist. Petr. | Giornale di Mineralogia, Cristallografia e Petrografia |
| Gironde Comm. Meteorol. | See Bordeaux Soc. Sci. Mem. |
| Gironde, J. Méd. | Journal Medical de la Gironde |
| Gistl, Faunus | Faunus |
| Glasgow. Inst. Engin. Trans. | Transactions of the Institution of Engineers and Shipbuilders in Scotland |
| Glasgow Med. Chir. Soc. Trans. | Transactions of the Medico-Chirurgical Society of Glasgow |
| Glasgow Med. J. | Glasgow Medical Journal |
| Glasgow Natur. Hist. Soc. Proc. & Trans. | Proceedings and Transactions of the Natural History Society of Glasgow |
| Glasgow Path. Clin. Soc. Trans. | Transactions of the Glasgow Pathological and Clinical Society |

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| Glasgow Phil. Soc. Proc. | Proceedings of the Philosophical Society of Glasgow |
| Glashütte | Glashütte, Die |
| Glas-Ind. | Glas-Industrie, Die |
| Gleanings Sci. | Gleanings in Science |
| Globe | See Geneve Soc. Geogr. Mem. |
| Glückauf | Glückauf; Berg- und Hüttenmannische-Zeitschrift |
| Good Roads | Good Roads |
| Goodsir, Ann. Anat. | Annals of Anatomy and Physiology |
| Physiol. | |
| Gordon Coll. Phot. Assoc. | See Wombat. |
| Görlitz, Abh. | Abhandlungen der Naturforschenden Gesellschaft zu Görlitz |
| Götheborg, Handl. | Götheborgs Kongl. Vetenskaps och Vitterhets Samhälles Handlingar |
| Götheborg, Nya Handl. | Nya Handlingar af Kongl. Vetenskaps och Vitterhets Samhället i Götheborg |
| Göttingen, Abh. | Abhandlungen der Königlichen Gesellschaft der Wissenschaften zu Göttingen |
| Göttingen, Comment. | Commentationes recentiores Societatis, etc. |
| Göttingen, Nachr. | Nachrichten von der Georg-Augusts Universität und der Königl. Gesellschaft der Wissenschaften zu Göttingen |
| Göttinger Studien | Göttinger Studien |
| Göttingen, Studien Ver. | Studien des Göttingischen Vereins Bergmännischer Freunde |
| Gräfe, J. Chir. Augenheilk. | Journal der Chirurgie und Augen-Heilkunde |
| Graph. Mitth. | Schweizer graphische Mittheilungen |
| Graubünden Naturf. Ges. Jahr. | Jahresbericht der Naturforschenden Gesellschaft Graubündens |
| Gravenhage, Athenaeum | Athenaeum |
| Gravenhage, Inst. Ingen. Tijdschr. | Tijdschrift van het Koninklijk Instituut van Ingenieurs |
| Gravenhage, Inst. Ingen. Uittrek. | Uittreksels uit Vreemde Tijdschriften voor de Leden van het Koninklijk Instituut van Ingenieurs |
| Gravenhage, Inst. Ingen. Verh. | Verhandelingen van het Koninklijk Instituut van Ingenieurs |
| Gravenhage, Inst. Ingen. Verslag. | K. Instituut van Ingenieurs. Algemeen Verslag van de Werkzaamheden en Notulen der Vergaderingen |
| Gravenhage, Tijdschr. | Tijdschrift voor Entomologie, door de Nederlandsche Entomologische Vereeniging |
| Graves, Natur. J. | The Naturalists' Journal and Miscellany |
| Graz Bot. Inst. Mitth. | Mittheilungen aus dem Botanischen Institute zu Graz |
| Graz, Unters. Physiol. Histol. | Untersuchungen aus dem Institute für Physiologie und Histologie |
| Great. Brit. Phil. Soc. | See Victoria Inst. J. |
| Greifswald Naturwiss. Ver. Mitth. | See Neu-Vorpommern Mitth. |
| Grenoble, Acad. Delph. Bull. | Bulletin de l'Académie Delphinale, ou Société des Sciences et Arts de Grenoble |
| Grevillea | Grevillea, a Quarterly Record of Cryptogamic Botany and its Literature |
| Groningen, Ann. Acad. | Annales Academiae Groninganae |
| Gruithuisen, Neue Analect. | Neue Analecten für Erd- und Himmelskunde |
| Brumert Archiv. | Archiv für Mathematik und Physik |
| Brumert, Meteor. Optik | Beiträge zur meteorologischen Optik, etc. |
| Guat. P. | Guatemala Patent |

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| Guia Minero | Guia del Minero: Periodico científico, industrial y mercantel |
| Guillemin Archiv. Bot. | Archives de Botanique, ou Recueil Mensuel de Memoires originaux, etc. |
| Gummi-Ztg. | Gummi-Zeitung |
| Günsburg, Zts. Klin. Med. | Zeitschrift für klinische Medizin, mit dem Verein für physiologische Heilkunde in Breslau |
| Gurlt, Mag. Ges. Thierheilk. | Magazin für die gesammte Thier-Heilkunde |
| Guy's Hosp. Rep. | Guy's Hospital Reports |
| Haarlem Kolon. Mus. Bull. | Bulletin van het Koloniaal Museum te Haarlem |
| Haarlem, Mus. Teyler Archiv. | Archives du Musee Teyler |
| Haarlem, Natuurk. Verh. Maatsch. Wet. | Natuurkundige Verhandelingen van de (Bataafsch) Hollandsche Maatschappij der Wetenschappente Haarlem |
| Haaxman, Tijdschr. | Tijdschrift voor Wetenschappelijke Pharmacie, etc. |
| Habana Acad. Anales. | Anales de la (Real) Academie de Ciencias Medicaes Fisicas y Naturales de la Habana |
| Haeser, Archiv. Med. | Archiv für die gesammte Medicin |
| Hage | See Gravenhage |
| Hahnemann, Month. | Hahnemannian Monthly, Philadelphia |
| Haidinger, Abh. | Naturwissenschaftliche Abhandlungen |
| Haidinger, Ber. | Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien |
| Hainaut Soc. Mem. | Memoires et Publications de la Société des Sciences, des Arts et des Lettres du Hainaut |
| Hall, Bijdragen | Bijdragen tot de Natuurkundige Wetenschappen |
| Halle, Abr. Naturwiss. Ver. | Abhandlungen des Naturwissenschaftlichen Vereins für Sachsen und Thüringen in Halle |
| Halle aux cuirs, La | Halle aux cuirs, La |
| Halle, Jahr. Naturwiss. Ver. | Jahresbericht des Naturwissenschaftlichen Vereins in Halle |
| Halle Kryptog. Lab. | See Beitr. Physiol. Morphol. |
| Halle, Naturf. Ges. Abh. | Abhandlungen der Naturforschenden Gesellschaft zu Halle |
| Halle, Naturf. Ges. Ber. | Bericht der Naturforschenden Gesellschaft zu Halle |
| Halle, Naturf. Ges. Neu. Schr. | Neue Schriften der Naturforschenden Gesellschaft zu Halle |
| Halle, Zts. Ges. Naturwiss. | Zeitschrift für die gesammten Naturwissenschaften |
| Hamburg, Abh. Geb. Naturwiss. | Abhandlungen aus dem Gebiete der Naturwissenschaften |
| Hamburg Bot. Ges. | See Bot. Centrbl. |
| Hamburg, Mitth. | Mittheilungen aus den Verhandlungen der Naturwissenschaftlichen Gesellschaft in Hamburg |
| Hamb. Mus. Ber. | Naturhistorisches Museum zu Hamburg. Berichte |
| Hamb. Mus. Jahr. | Jahresbericht über das Naturhistorische Museum zu Hamburg |
| Hamb. Mus. Mitth. | Mittheilung aus dem Naturhistorischen Museum in Hamburg |
| Hamb. Naturwiss. Ver. Abh. | Abhandlungen aus dem Gebiete der Naturwissenschaften herausgegeben vom Naturwissenschaftlichen Verein in Hamburg |
| Hamb. Ver. Naturwiss. Unterh. Verh. | Verhandlungen des Vereins für Naturwissenschaftliche Unterhaltung zu Hamburg |
| Hamb. Wiss. Anst. Jahr. | Jahrbuch der Hamburgischen Wissenschaftlichen An- |

- Hampshire Field Club Pap. & Proc. Papers and Proceedings of the Hampshire Field Club
- Hannover Architect.-Ver. Zts. Zeitschrift des Architekten- und Ingenieur-Vereins zu Hannover. Zeitschrift für Architektur und Ingenieurwesen
- Hannover Jahr. ... Jahresbericht der Naturhistorischen Gesellschaft zu Hannover
- Hannöversiche Ann. Hannöversiche Annalen für die gesammte Heilkunde
- Harlem Soc. Holland. Sci. See Arch. Neerland
- Hartford, Trans. Transactions of the Natural History Society of Hartford
- Harvard Mus. Zool. Mem. Memoirs of the Museum of Comparative Zoology at Harvard College
- Harvard Mus. Zool. Bull. Bulletin of the Museum of Comparative Zoology at Harvard College, in Cambridge
- Harz, Naturwiss. Ver. Ber. Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
- Havre, Cercle Bot. Cercle pratique d'Horticulture et de Botanique de l'arrondissement du Havre: Bulletins
- Haw. P. Hawaiian Patent
- Haye See Congr. Int. Hyg. C. R., 1884
- Heart Heart
- Hedwigia Hedwigia. Ein Notizblatt für Kryptogamische Studien nebst Repertorium für Kryptogamische Literatur. Hedwigia. Organ für (specielle) Kryptogamenkunde (und Phytopathologie) nebst Repertorium für (Kryptogamische) Literatur.
- Heidelb. Jahr. Lit. Jahrbücher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
- Heidelb. Naturhist. Med. Festschr. Festschrift zur Feier des fünfshundertjährigen Bestehens der Rupe-to-Carola dargebracht von dem Naturhistorisch-Medicinischen Verein zu Heidelberg
- Heidelb. Naturhist. Med. Verh. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
- Heidelb., Verh. Verhandlungen der in Heidelberg versammelten Augenärzte
- Heis, Wochenschr. Wochenschrift für Astronomie, Meteorologie, und Geographie
- Heller, Archiv. Archiv für physiologische und pathologische Chemie und Mikroskopie
- Helsingfors, Acta Soc. Sci. Fenn. Acta Societatis Scientiarum Fennicae
- Helsingfors, Bidrag Finlands Natur o. Folk. Bidrag till kännedom om Finlands Natur och Folk, utgifna af Finska Vetenskaps-Societeten
- Helsingfors, Bidrag Finlands Naturkänn. Statistik, utgifna af Finska Vetenskaps-Societeten
- Helsingfors, Faun. Flor. Acta Societatis pro Fauna et Flora Fennica
- Fenn. Acta.
- Helsingfors, Fauna Flora Medd. Meddelanden af Societas pro Fauna et Flora Fennica
- Fenn. Medd.
- Helsingfors, Faun. Flor. Notiser ur Sällskapet pro Fauna et Flora Fennica
- Fenn. Notiser Förhandlingar
- Helsingfors, Öfvers, Finaka Vet. Soc. Öfversigt af Finska Vetenskaps-Societätens Förhandlingar
- Helv. Chim. Acta Helvetica Chimica Acta
- Henle und Pfäfer, Zts. See Zeitschrift für rationelle Medicin
- Hermannstader Verh. Verhandlungen und Mittheilungen des Siebenbürgischen Vereins für Naturwissenschaften in Hermannstadt

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| Hermbstätt, Archiv. | Archiv der Agriculturchemie für denkende Landwirthe |
| Hermstätt, Bull. | Bulletin des Neuesten und Wissenwürdigsten aus der Naturwissenschaft, etc. |
| Hermbstätt, Museum | Museum des Neuesten und Wissenwürdigsten aus dem Gebiete der Naturwissenschaft, der Künste, der Fabriken, der Manufakturen, der technischen Gewerbe, der Landwirthschaft, der Produktenwaaren und Handelskunde, und der bürgerlichen Haushaltung, &c. |
| Hertha | Hertha |
| Herts. Natur. Hist. Soc. Trans. | Transactions of the Hertfordshire Natural History Society and Field Club |
| Hessen, Naturhist. Verg. | Verhandlungen des Naturhistorischen Vereins für das Gross herzogthum Hessen und Umgebung |
| Heusinger, Zts. | Zeitschrift für die organische Physik |
| Hide and Leather | Hide and Leather |
| High Wycombe Natur. Hist. Mag. | The Quarterly Magazine of the High Wycombe Natural History Society |
| Highland Soc. Trans. | Transactions of the Highland and Agricultural Society of Scotland with an abstract of the Proceedings |
| Hildesheim, Roemer-Mus. Mitth. | Mittheilungen aus dem Roemer-Museum Hildesheim |
| Himly, Bibl. Ophthalm. | Bibliothek für Ophthalmologie |
| Hippone | See Bone |
| Hisinger, Afh. | Afhandlingar i Fysik, Kemi, och Mineralogie |
| Hobart Town | See Tasmania |
| Hoeven en Vriese, Tijdschr. | Tijdschrift voor Natuurlijke Geschiedenis en Physiologie |
| Hoff, Mag. | Magazin für die gesammte Mineralogie, Geognosie, etc. |
| Hoffman, Phytogr. Blätt. | Phytographische Blätter |
| Holl. P. | Holland Patent |
| Holländ, Beitr. | Holländische Beiträge zu den anatomischen und physiologischen Wissenschaften |
| Holländ, Mag. | Holländisches Magazin der Naturkunde |
| Holmesdale Natur. Hist. Club Proc. | Proceedings and Annual Reports of the Holmesdale Natural History Club, Reigate, for the years 1865-67 |
| Homme | L'Homme: Journal illustre des Sciences Anthropologiques |
| Hooker, Bot. Miscell. | The Botanical Miscellany |
| Hooker, Comp. Bot. Mag. | Companion to the Botanical Magazine |
| Hooker, Lond. J. Bot. | London Journal of Botany |
| Hoppe, Bot. Taschenb. | Neues Botanisches Taschenbuch für die Anfänger dieser Wissenschaft und der Apothekerkunst |
| Horae Soc. Entom. Rossicae | Horae Societatis Entomologicae Rossicae variis sermonibus Rossicae usitatis |
| Horkel, Archiv. | Archiv. für die thierische Chemie |
| Horn, Archiv. Med. | Archiv. für praktische Medizin und Klinik |
| Horn's Phot. J. | Horn's photographisches Journal |
| Hornschuch, Archiv. | Archiv Skandinavischer Beiträge zur Naturgeschichte |
| Horolog. J. | The Horological Journal |
| Hortic. Soc. J. | Journal of the Royal Horticultural Society of London |
| Hortic. Soc. Trans. | Transactions of the Horticultural Society of London |
| Hufeland, J. Arzn. | Journal der practischen Arzneikunde |
| Humboldt. | Humboldt. Monatsschrift für die Gesammten Naturwissenschaften |
| Humming Bird | The Humming Bird. . . . scientific, artistic and industrial Review |

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| Hongkong P. | Hongkong Patent |
| Hung. P. | Hungarian Patent |
| Hutm. Ztg. | Deutsche Hutmacher-Zeitung |
| Hyg. Congr. | See Congr. Int. Hig. Act.; Congr. Int. Hyg. C. R.; Int. Congr. Hyg. Arb.; Int. Congr. Hyg. Trans. |
| Hyg. Rundschau. | Hygienische Rundschau. Berlin |
| Hyg. viande | Hygiène de la viande et du lait, I' |
| Iekaterinenb., Soc. Oural. | Bulletin de la Société Ouralienne d'Amateurs des |
| Bull. | Sciences Naturelles |
| Il Berico | Il Berico |
| Il Cimento | Il Cimento |
| Il Giamb-Vico | Il Giambattista-Vico |
| Il Progresso | Il Progresso delle Scienze, Lettere, ed. Arti. |
| Il Subalpino | Il Subalpino, Giornale di Scienze |
| Il Tempo | Il Tempo, Giornale Italiano di Medicina |
| III. Insects Rep. | ... Report of the State Entomologist... on the Noxious and Beneficial Insects of the State of Illinois |
| III. Lab. Natur. Hist. Bull. | Bulletin of the Illinois State Laboratory of Natural History |
| III. Mus. Natur. Hist. Bull. | Bulletin... of the Illinois State Museum of Natural History |
| Illiger, Magazin | Magazin für Insektenkunde |
| Illumin. Engin. (London) | Illuminating Engineer (London), The |
| Illust. Hortic. | Illustration horticole; journal special des Serres et des Jardins |
| Illust. landw. Ztg. | Illustrierte landwirtschaftliche Zeitung |
| Illust. Off. J. | Illustrated Official Journal, The (Patents) |
| Illust. Wochenschr. Entom. | Illustrierte Wochenschrift für Entomologie. Inter- nationales Organ für alle Interessen der Insekten- kunde. Offizielles Organ der Berliner Entomolo- gischen Gesellschaft |
| Impr. | L'imprimerie |
| Ind. Chim. | Industria chimica |
| Ind. lait. | L'Industrie laitière |
| Ind. Text. | L'industrie textile |
| Ind. Ztg. | Deutsche Industrie Zeitung |
| Index Med. | Index Medicus, Washington |
| India Agric. Soc. J. | Journal of the Agricultural and Horticultural Society of India |
| India, Agric. Soc. Proc. | Proceedings of the Agricultural and Horticultural Society of India |
| India Agric. Soc. Trans. | Transactions of the Agricultural and Horticultural Society of India |
| India Bot. Surv. Records | Records of the Botanical Survey of India |
| India Dept. Agric. | India Department of Agriculture, Publications |
| India, Govt. Records (For. Dept.) | Selections from the Records of the Government of India. (Foreign Department) |
| India, Govt. Records (Home Dept.) | Selections from the Records of the Government of India |
| India P. | Indian Patent |
| India Rev. | India Review and Journal of Foreign Science and the Arts |
| India Rub. J. | India Rubber Journal |
| India Rub. World | India Rubber World |
| Indian Ann. | Indian Annals of Medical Science |
| Indian J. Med. Phys. Sci. | Indian Journal of Medical Science |
| Indian Med. Gaz. | The Indian Medical Gazette, a monthly record of Medicine, &c. |

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| Indian Meteorol. Mem. | Indian Meteorological Memoirs: being occasional Discussions and Compilations of meteorological data relating to India and the neighboring countries |
| Indian Mus. Notes | Indian Museum Notes |
| Industrieztg. Ungarn | Industriezeitung für Ungarn |
| Ingenieur | Der Ingenieur |
| Inghirami, Opuscoli | Nuova Collezione di Opuscoli e Notizie di Scienze |
| Innsbruck, Jahr. | Jahresbericht der k. k. Ober-Realschule zu Innsbruck |
| Innsbruck Naturwiss. | Berichte des Naturwissenschaftlich-medizinischen Vereines in Innsbruck |
| Med. Ber. | Neue Zeitschrift des Ferdinandeums für Tirol |
| Innsbruck, Neue Zts. | Zeitschrift des Ferdinandeums für Tirol und Voralberg |
| Innsbruck, Zts. Ferdinandeums | |
| Inst. | L'Institut |
| Inst. Act. J. | Journal of the Institute of Actuaries (and Assurance Magazine) |
| Inst. Brewing Trans. | Transactions of the Institute of Brewing |
| Inst. Civ. Eng. Proc. | Minutes of the Proceedings of the Institution of Civil Engineers |
| Inst. Egypt. Bull. | Bulletin de l'Institut Egyptien |
| Inst. Egypt. Mem. | Memoires (ou Travaux originaux) presentes (et lus) a l'Institut Egyptien |
| Inst. Elect. Engin. J. | Journal of the Institution of Electrical Engineers |
| Inst. Mechan. Engin. Proc. | Institution of Mechanical Engineers. Proceedings |
| Inst. Min. Eng. Trans. | Transactions of the Institution of Mining Engineers |
| Inst. Min. Met. Trans. | Transactions of the Institution of Mining and Metallurgy |
| Inst. Solvay Trav. | Institut Solvay. Travaux de Laboratoire |
| Intell. Observer | The Intellectual Observer |
| Intl. Beitr. Path. Therap. | Internationale Beiträge zur Pathologie und Therapie, die Ernährungsstörungen, Stoffwechsel und Verdauungskrankheiten |
| Intl. Congr. Appl. Chem. | International Congress of Applied Chemistry |
| Intl. Congr. Hyg. Trans. | Transactions of the International Congress of Hygiene and Demography |
| Intl. Congr. Zool. Proc. | Proceedings International Congress of Zoology |
| Intl. Entom. Ver. | See Zürich, Soc. Ent. |
| Intl. Med. Congr. Trans. | Transactions of the International Medical Congress |
| Intl. Med. Congr. Verh. | Verhandlungen des Internationalen Medicinischen Congresses |
| Intl. J. Anat. | Monthly International Journal of Anatomy and Histology (Physiology) |
| Intl. Mschr. Anat. | See Intl. J. Anat. |
| Intl. Sugar J. | International Sugar Journal, The |
| Intl. Zentr. Baukeram. Glasind. | Internationales Zentralblatt für Baukeramik und Glasindustrie |
| Intl. Zts. Metallog. | Internationale Zeitschrift für Metallographie |
| Invent. Rec. | Inventor's Record, The |
| Iowa Acad. Sci. Proc. | Proceedings of the Iowa Academy of Sciences |
| Iowa Univ. Lab. Natur. Hist. Bull. | Bulletin from the Laboratories of Natural History of the State University of Iowa |
| Ireland, Coll. Physicians Trans. | Transactions of the Association of Fellows and Licentiates of the King's and Queen's College of Physicians in Ireland |
| Ireland, Inst. Civ. Eng. Trans. | The Transactions of the Institute of Civil Engineers of Ireland |

- Ireland Roy. Soc. Ant. See Dublin, Roy. Soc. Ant. Ir. Jl.
 Proc. & Pap.
 Ireland Zool. Soc. See Irish Natlist
 Iris • Correspondenz-Blatt des Entomologischen Vereins
 Iris zu Dresden. Iris, Dresden. Deutsche Entomologische Zeitschrift herausgegeben von der Gesellschaft Iris zu Dresden in Verbindung mit der Deutschen Entomologischen Gesellschaft zu Berlin. .
 Fortsetzung des "Correspondenz-Blattes des Entomologischen Vereins Iris."
 Irish Acad. Cunningham Royal Irish Academy. •Cunningham Memoirs
 Mem.
 Irish Acad. Proc. Proceedings of the Royal Irish Academy
 Irish Acad. Trans. The Transactions of the Royal Irish Academy
 Irish Natur. The Irish Naturalist: a monthly Journal of general Irish Natural History
 Iron Iron
 Iron Age Iron Age
 Iron Coal Trades Rev. Iron Coal Trades Review
 Iron Steel Inst. J. The Journal of the Iron & Steel Institute
 Iron Steel Inst. Trans. Transactions of the Iron and Steel Institute
 Isenflam, Beitr. Zerglied. Beiträge für die Zergliederungskunst
 Isere Soc. Bull. Bulletin de la Société de Statistique, des Sciences naturelles et des Arts industriels du Département de l'Isere
 Isle of Man Natur. Hist. & See Yn Lioar Manninagh
 Antiq. Soc.
 Ital. P. Italian Patent
 Italia, Soc. Bot. Bull. Bullettino della Societa Botanica Italiana
 Italia Soc. Crittog. Atti Atti della Societa Crittogamologica Italiana
 Italia Soc. Crittog. Comment. Commentario della Societa Crittogamologica Italiana
 Italia Soc. Crittog. Mem. Memorie della Societa Crittogamologica Italiana
 Italia, Soc. Entom. Bull. Bullettino della Societa Entomologica Italiana
 Italia, Soc. Zool. Boll. Bollettino della Societa Zoologica Italiana
 Ithaca, Cornell Univ. Bull. Bulletins of American Paleontology
 Amer. Paleont.
 J. Journal
 J. A. C. S. Journal of the American Chemical Society
 J. Adv. Therap. Journal of Advanced Therapeutics, New York
 J. Agric. The (Quarterly) Journal of Agriculture
 J. agric. Hort. Journal de l'Agriculture, le Horticulture, etc.
 J. Agric. Prat. Journal d'Agriculture pratique, etc.
 J. Agric. Sci. Journal of Agricultural Science
 J. agric. Soc. Journal of the Agricultural Society
 J. Agric. Tropicale Journal d'Agriculture tropicale
 J. allied Soc. Journal of the Allied Societies (Dental)
 J. Amer. Lea. Chem. Assoc. Journal of the American Leather Chemists' Association
 J. Amer. Med. Assoc. Journal of the American Medical Association
 J. Amer. Pharm. Assoc. Journal of the American Pharmaceutical Association
 J. Amer. Soc. Mechan. Eng. Journal of the American Society of Mechanical Engineers
 J. Anal. Chem. The Journal of Analytical (and Applied) Chemistry
 J. Anat. Journal de l'anatomie de la Physiologie normales et pathologiques de l'homme et des animaux
 J. Anat. Physiol. The Journal of Anatomy and Physiology
 J. Appl. Chem. Journal of Applied Chemistry

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| J. Appl. Micr. | Journal of Applied Microscopy |
| J. Assoc. Eng. Soc. | Journal of the Association of Engineering Societies |
| J. Biol. Chem. | Journal of Biological Chemistry |
| J. Bot. | Journal de Botanique |
| J. Buchdr. | Journal für Buchdruckerkunst |
| J. C. S. | Journal of the Chemical Society, London |
| J. Camera Club | Journal of the Camera Club |
| J. Can. Min. Inst. | Journal of the Canadian Mining Institutes |
| J. Chem. Met. Soc. South Af. | Journal of the Chemical, Metallurgical and Mining Society of South Africa |
| J. chim. med. | Journal de chimie medicale, de pharmacie et de toxicologie |
| J. chim. phys. | Journal de chimie, physique, electrochimie, thermo-chimie, radiochimie, mecanique, chimie, stoichiometrie |
| J. Chir. | Journal de Chirurgie |
| J. Chir. Augenheilk. | Journal der Chirurgie und Augenheilkunde |
| J. Coll. Agric. Imp. Univ. Tokyo | Journal of the College of Agriculture, Imperial University of Tokyo |
| J. Comp. Path. Therap. | The Journal of Comparative Pathology and Therapeutics |
| J. Conch. | The Journal of Conchology |
| J. ecole poly. | Journal de l'Ecole polytechnique |
| J. Entom. | Journal of Entomology, descriptive and geographical |
| J. Exp. Med. | Journal of Experimental Medicine |
| J. Exp. Zool. | Journal of Experimental Zoology, The |
| J. fabr. sucre | Journal des fabricants de sucre |
| J. Frank. Inst. | Journal of the Franklin Institute |
| J. Gasbeleucht | Journal für Gasbeleuchtung |
| J. Gaslighting | Journal of Gas Lighting |
| J. Gen. Physiol. | Journal of General Physiology |
| J. Genie Civ. | Journal du Genie Civil des Sciences et des Arts |
| J. Geol. | Journal of Geology |
| J. Goldschm. | Journal der Goldschmiedekunst und verwandter Gewerbe |
| J. Heb. Med. | Journal Hebdomadaire de Medecine |
| J. Heb. Sci. Med. | Journal Hebdomadaire des Progres des Sciences et Institutions Medicales |
| J. Home Econ. | Journal of Home Economics, The |
| J. Hygiene | Journal of Hygiene |
| J. Ind. Eng. Chem. | Journal of Industrial and Engineering Chemistry |
| J. Indian Archipel. | Journal of the Indian Archipelago and Eastern Asia |
| J. Infect. Dis. | Journal of Infectious Diseases |
| J. Inst. Brewing | Journal of the Institute of Brewing |
| J. Inst. Metals | Journal of the Institute of Metals |
| J. Intl. Anat. | See Int. J. Anat. |
| J. Invent. | Journal des Inventeurs |
| J. Landw. | Journal für Landwirtschaft |
| J. Med. Chir. Pharm. | Journal de Medecine, Chirurgie, Pharmacie |
| J. Med. Paris | Journal de medecine de Paris |
| J. Med. Research | Journal of Medical Research |
| J. Microgr. | Journal de micrographie |
| J. Micro. Sci. | Quarterly Journal of Microscopical Science |
| J. Mines | Journal des Mines, ou Recueil de Memoires sur l'exploitation des Mines, et sur les Sciences et les Arts qui s'y rapportent |
| J. mines met. | Journal des mines et de metallurgie |
| J. Morphol. | Journal of Morphology |

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| J. Mus. Godeffroy | Journal des Museum Godeffroy. Geographische, Ethnographische und Naturwissenschaftliche Mittheilungen |
| J. Mycol. | The Journal of Mycology |
| J. N. Engl. Water Works Assoc. | Journal New England Water Works Association |
| J. Ophthalmol. | Journal d'Ophthalmologie |
| J. Ornith. | Journal für Ornithologie |
| J. Papier | Journal de Fabricants de Papier, fonde et publie par L. Piette |
| J. Path. Bact. | The Journal of Pathology and Bacteriology |
| J. Petrole | Journal du petrole |
| J. Pharm. | Journal de Pharmacie |
| J. Pharm. Anvers | Journal de Pharmacie d'Anvers |
| J. Pharm. Chim. | Journal de Pharmacie et de Chimie |
| J. Pharm. Elsass-Lothringen | Journal de pharmacie von Elsass-Lothringen |
| J. Pharm. Soc. Japan | Yakagakuzasshi (Journal of the pharmaceutical society of Japan) |
| J. Pharmacol. | Journal of Pharmacology and Experimental Therapeutics |
| J. Phot. Suppl. | Journal of Photographic Supplies |
| J. Phot. Soc. | Journal of the Photographic Society |
| J. Phys. | Journal de Physique theorique et appliquee |
| J. Phys. Chem. | The Journal of Physical Chemistry |
| J. Phys. Chim. | Journal de Physique, de Chimie, et de l'Histoire Naturelle |
| J. Physiol. | The Journal of Physiology |
| J. physiol. path. gen. | Journal de physiologie et de pathologie general, Paris |
| J. prakt. Chem. | Erdmann's Journal für praktische Chemie |
| J. Psychol. Med. | Journal of Psychological Medicine and Mental Pathology |
| J. Roy. Agric. Soc. | Journal of the Royal Agricultural Society |
| J. Roy. Astron. Soc. Canada | Journal of the Royal Astronomical Society of Canada |
| J. Roy. Inst. Pub. Health | Journal of the Royal Institute of Public Health |
| J. Roy. San. Inst. | Journal of the Royal Sanitary Institute |
| J. Roy. Soc. N. S. Wales | Journal of the Royal Society of New South Wales |
| J. Roy. U. S. Inst. | Journal Royal United Service Institution |
| J. Russ. Phys. Chem. Soc. | Journal of the Russian Physical Chemical Society |
| J. S. C. I. | Journal of the Society of Chemical Industry |
| J. Savants | Journal des Savants |
| J. Sci. | The Journal of Science |
| J. sci. math. phys. nat. | Journal de ciencias mathematicas, physicas naturales |
| J. Soc. Arts | Journal of the Royal Society of Arts |
| J. Soc. Dyers Col. | Journal of the Society of Dyers and Colorists |
| J. soc. pharm. Anvers | Journal de pharmacie, organe de la société de pharmacie d'Anvers |
| J. Soc. Electr. Eng. | Journal of the Society of Telegraphic Engineers |
| J. State Med. | The Journal of State Medicine |
| J. suisse chim. pharm. | Journal suisse de chimie et pharmacie |
| J. Travel | The Journal of Travel and Natural History |
| J. Trop. Med. | The Journal of Tropical Medicine |
| J. U. S. Artill. | Journal of the United States Artillery |
| J. Univ. Med. | Journal universel et hebdomadaire de Medecine et de Chirurgie pratiques et des Institutions medicales |
| J. Univ. Sci. Med. | Journal Universel des Sciences Medicales |
| J. Wash. Acad. Sci. | Journal of the Washington Academy of Sciences |
| J. Western Soc. Eng. | Journal of the Western Society of Engineers |

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| Jaarb. Mijnw. Nederl. Ind. | Jaarboek van het Mijnwesen in Nederlandsch Oost-Indie |
| Jahr. 4 Jahresbericht | Jahrbuch |
| Jahr. Agrik.-Chem. | Jahresbericht über die Fortschritte der Agrikulturchemie mit besonderer Berücksichtigung der Pflanzenchemie und Pflanzenphysiologie |
| Jahr. Berg- u. Hüttenw. | Jahrbuch für das Berg- und Hüttenwesen im Königreiche Sachsen |
| Jahr. Kinderheilk. | Jahrbuch für Kinderheilkunde und physische Erziehung |
| Jahr. Chem. | Jahresbericht der Chemie (Liebig-Kopp) |
| Jahr. Gähr. Organ. | Jahresbericht über die Fortschritte in der Lehre von den Gährungs-Organismen (Koch) |
| Jahr. Mineral. | Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie |
| Jahr. Mineral Beil.-Bd. | Neues Jahrbuch für Mineralogie, Geologie, und Palaeontologie, Beilage-Band |
| Jahr. Pharm. | Jahresbericht der Pharmacie |
| Jahr. Phot. | Jahrbuch der Photographie (Eder) |
| Jahr. Phot. Reprod. | Jahrbuch für Photographie und Reproduktionstechnik |
| Jahr. Phy. Ver. Frankfurt | See Frankfurt, Jahr. Phys. Ver. |
| Jahr. Physiol. | Jahresbericht über die Fortschritte der Physiologie |
| Jahr. Radioactiv. Electronik. | Jahrbuch der Radioaktivität und Electronik |
| Jahr. rein. Chem. | Jahresbericht der reinen Chemie |
| Jahr. Tier-Chem. | Jahresbericht über der Fortschritte der Tier-Chemie |
| Jahr. wiss. Bot. | Jahrbücher für wissenschaftliche Botanik |
| Jamaica Inst. J. | Journal of the Institute of Jamaica |
| Jamaica P. | Jamaica Patent |
| Jamaica Soc. Arts. Trans. | Transactions of the Jamaica Society of Arts |
| Jamain, Archives Ophthalm. | Archives d'Ophthalmologie |
| Jap. P. | Japanese Patent |
| Jardine, Mag. Zool. Bot. | The Magazine of Zoology and Botany |
| Jena Ann. Acad. | Annales Academiae Jenensis |
| Jena Ann. Phys. Med. | Die Jenaischen Annalen für Physiologie und Medicin |
| Jena Ann. Soc. Mineral | Annalen der Societät für die gesammte Mineralogie zu Jena |
| Jena Denkschr. | Denkschriften der Medicinisch-Naturwissenschaftlichen Gesellschaft zu Jena |
| Jena Geogr. Ges. Mitth. | Mittheilungen der geographischen Gesellschaft (für Thüringen) zu Jena |
| Jena Sitzber. | Sitzungsberichte der Jenaischen. Gesellschaft für Medicin und Naturwissenschaft |
| Jena Zts. | Jenaische Zeitschrift für Naturwissenschaft herausgegeben von der Medicinisch-naturwissenschaftlichen Gesellschaft zu Jena |
| Jern-Kontoret's Ann. | Jern-Kontoret's Annaler |
| Johns Hopkins Biol. Lab. Mem. | Memoirs from the biological laboratory of the Johns Hopkins University |
| Johns Hopkins Biol. Lab. Stud. | Johns Hopkins University. Studies from the Biological Laboratory |
| Johns Hopkins Univ. Circ. | The Johns Hopkins University Circulars |
| Jura, Trav. Soc. Emul. | Travaux de la Société d'Émulation du Department du Jura |
| Jurjew | See Dorpat |
| Just's bot. Jahr. | Just's botanischer Jahresbericht, Leipzig and Berlin |
| Kali | Kali |

LIST OF ABBREVIATIONS TO LITERATURE

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| Kampen, Mag. | Magazin voor Wetenschappen, Kunsten, &c. |
| Kan. Acad. Sci. Trans. | Transactions of the . . . annual meeting of the Kansas Academy of Science |
| Kans. Univ. Quart. | The Kansas University Quarterly |
| Karlsruhe Bact. Inst. Arb. | Arbeiten aus dem bacteriologischen Institut der technischen Hochschule zu Karlsruhe |
| Karlsruhe Naturwiss. Ver. Verh. | Verhandlungen des Naturwissenschaftlichen Vereins in Karlsruhe |
| Kärnten, Berg-Verein, Zts. | Zeitschrift des Berg- u. Hüttenmännischen Vereins für Kärnten |
| Kärnten Landesmus. Jahr. | Jahrbuch des naturhistorischen Landes-Museums von Kärnten |
| Kärnten, Zts. | Zeitschrift des berg- und hüttenmännischen Vereines für Kärnten |
| Karsten | See Botan. Untersuch. |
| Karsten, Archiv. | Archiv für Mineralogie, Geognosie, Bergbau, und Hüttenkunde |
| Kassel Ver. Naturk. Ber. | Bericht des Vereins für Naturkunde zu Cassel |
| Kassel Ver. Naturk. Festschr. | Festschrift des Vereins für Naturkunde zu Cassel zur Feier seines Fünfzigjährigen Bestehens |
| Kastner, Archiv. Chem. | Archiv. für Chemie und Meteorologie |
| Kastner, Archiv. Naturlehre | Archiv. für die gesammte Naturlehre |
| Kazan Soc. Phys.-Math. Bull. | Bulletin de la Société Physico-Mathématique de Kazan |
| Kazan Soc. Natur. Proc. | Proceedings of the Physico-Mathematical Section of the Society of Naturalists of the Imperial University of Kazan |
| Kazan Soc. Natur. Trans. | Transactions of the Society of Naturalists of the Imperial University of Kazan |
| Kazan Univ. Bull. | Bulletin of the Imperial University of Kazan |
| Kazan Univ. Mem. | Scientific Memoirs of the Imperial University of Kazan |
| Kekule, Krit. Zts. Chem. | Kritische Zeitschrift für Chemie, Physik, und Mathematik; see also Zts. Chem. |
| Keram. Rundschau | Keramische Rundschau |
| Kew Bull. | Royal (Botanic) Gardens, Kew. Bulletin of Miscellaneous Information |
| Kharkov. Math. Soc. Commun. | Communications de la Société Mathématique de Kharkov |
| Kiel. Mitth. Ver. Elbe. | Mittheilungen des Vereins nördlich der Elbe zur Verbreitung naturwissenschaftlicher Kenntnisse in Kiel |
| Kiel, Physiol. Inst. Arb. | Arbeiten aus dem Kieler physiologischen Institut |
| Kiel, Schr. | Schriften der Universität zu Kiel |
| Kiel Univ. Mineral. Inst. Mitth. | Mittheilungen aus dem Mineralogischen Institut der Universität Kiel |
| Kiev Soc. Natur. Mem. | Memoires de la Société des Naturalistes de Kiev |
| Kjöbenh. Bot. For. | See Bot. Tidsskr. |
| Kjöbenh. Bot. For. Festskr. | Festskrift, udgivet af den Botaniske Forening i Kjöbenhavn i Anledning af dens Halvhundredaars fest, den 12 April, 1890 |
| Kjöbenh. Bot. For. Medd. | Meddelelser fra den Botaniske Forening i Kjöbenhavn |
| Kjöbenh. Carlsb. Lab. Medd. | Meddelelser fra Carlsberg Laboratoriet |
| Kjöbenh. Dansk. Vid. Selsk. Afh. | Det Kongelige Danske Videnskabernes Selskabs naturvidenskabelige og matematiske Afhandlinger |

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| Kiöbenh., Dansk. Vid. Selsk. Skrift. | Det Kongelige Danske Videnskabernes Selskabs Skrifter. Naturvidenskabelig og Mathematisk Afdeling |
| Kiöbenh. Ent. Fof. | See Ent. Medd. (Kiöbenh.) |
| Kiöbenh., Oversigt | Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger og dets Medlemmers Arbejder i Aaret 1874(-83) . . . samt. med en Résumé du Bulletin de l'Académie Royale Danoise des Sciences et des Lettres pour l'année 1874(-83) |
| Kiöbenh., Reg. Soc. Med. Acta. | Acta Regiae Societatis Medicae Havniensis |
| Kiöbenh., Vidensk. Forh. | Videnskabelige Forhandlinger ved Siølland Stifts Landemøde |
| Kiöbenh, Vidensk. Meddel. | Videnskabelige Meddelelser fra den Naturhistoriske Forening i Kjöbenhavn |
| K. K. Ges. Aerzte, Klausenburg | See Med. Jahr. |
| Kliniek | See Kolozsvár |
| Klug, Jahr. Insect. | Kliniek |
| Koll. Chem. Beihefte | Jahrbücher der Insectenkunde, etc. |
| Kolloid-Zts. | Kolloidchemische Beihefte |
| Kolozsvár Orvos-Termesz. Tars. Ertes. | Kolloid-Zeitschrift |
| | Ertesitő a "Kolozsvári Orvos-Termesztudományi Társulat"-nak az . . . orvosi, természetstudományi szaküléseiről Proceedings of the Medical and natural history sections of the Klausenburg Medical and Natural History Society |
| K. Svenska Vet.-Akad. Königsb. Archiv. | Kongl. Svenska Vetenskaps-Akademiens Handlingar |
| Königsb. Med. Jahr. | Königsberger Archiv für Naturwissenschaften und Mathematik |
| Königsb. Schr. | Königsberger medicinische Jahrbücher; herausgegeben von dem Verein für wissenschaftliche Heilkunde zu Königsberg |
| Kosmos (Lwow) | Schriften der physikalisch-ökonomischen Gesellschaft zu Königsberg in Preussen |
| Krain Mus.-Ver. Mitth. | K o s m o s, Czasopismo polskiego Towarzystwa przyrodników imienia Kopernika. (Cosmos. The Journal of the Polish Society Naturalists founded in honor of Copernicus) |
| Krakow Akad. (Mat.-Przyrod) Pam. | See Laibach, Mus.-Ver. Krain Mitth. |
| Krakow Akad. (Mat.-Przyrod) Rozpr. | Pamiętnik Akademii Umiejętności w Krakowie. Wydział Matematyczno-Przyrodniczy. (Memoires of the Academy of Science in Cracow. Section of Mathematics and Natural Science) |
| | Rozprawy i Sprawozdania z Posiedzeń Wydziału Matematyczno-Przyrodniczego Akademii Umiejętności. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science) |
| Krakow, Akad. (Mat.-Przyrod.) Rozpr. & Spraw. | Rozprawy i Sprawozdania z Posiedzeń Wydziału Matematyczno-Przyrodniczego Akademii Umiejętności. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science) |
| Krakow Kom. Fizyogr. Spraw. | Akademija Umiejętności w Krakowie. Sprawozdanie Komisji Fizyograficznej (Academy of Science in Cracow. Report of the Physiographical Commission) |
| Krakow, Roczn. Tow. Nauk. | Rocznik Towarzystwa Naukowego z Uniwersytetem Jagiellońskim Złączonego |
| Krakau, Untersuch. Path. Anat. | Untersuchungen aus dem Pathologisch-Anatomischen Institute in Krakau |

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| Kreutzer's Jahr. Phot. | Kreutzer's Jahresbericht der Photographie |
| Kristiania, Geogr. Selsk. Arb. | Det Norske Geografiske Selskabs Årbog |
| Kristiania, Norw. Mar. Investig. Rep. | Report on Norwegian Fishery and Marine Investigations |
| Kroyer, Naturhist. Tidssk. | Naturhistorisk Tidsskrift |
| Kühn-Archiv. | Kühn-Archiv. (formerly Berichte aus dem physiologischen Laboratorium und der Versuchsanstalt des Landwirtschaftlichen Instituts der Universität Halle) |
| Kult. Ing. | Der Kultur-Ingenieur (F. Dünkelberg) |
| Kunst. | Kunststoffe |
| Lab. Club. Trans. | Transactions of the Laboratory Club |
| Laboratory | The Laboratory |
| Laibach, Jahr. Gymnas. | Jahresbericht des k. k. Ober-Gymnasiums in Laibach |
| Laibach, Jahr. Realschule | Jahresbericht der k. k. selbständigen Unter-Realschule zu Laibach |
| Laibach, Jahresh. | Jahresheft des Vereins des Krainischen Landes Museums in Laibach |
| Laibach, Mus.-Ver. Krain Mitth. | Mittheilungen des Museal-Vereins für Krain |
| Lancet | The Lancet, London |
| Landb. Cour. | Landbouw-Courant |
| Landshut Bot. Ver. Ber. | Bericht des Botanischen Vereines in Landshut |
| Landw. Centr. | Landwirtschaftliches Centralblatt für Deutschland |
| Landw. Jahr. | Landwirtschaftliche Jahrbücher. Zeitschrift für wissenschaftliche Landwirtschaft und Archiv des Königlich Preussischen Landes-Oekonomie-Kollegiums |
| Landw. Jahr. Schweiz | Landwirtschaftliches Jahrbuch der Schweiz |
| Landw. Presse | Landwirtschaftliche Presse |
| Landw. Versuchs-Stat. | Die landwirtschaftlichen Versuchs-Stationen |
| Landw. Ztg. | Landwirtschaftliche Zeitung |
| Laon, Soc. Acad. Bull. | Bulletin de la Société Académique de Laon |
| Laurent Ann. Anat. | Annales Françaises et Étrangères d'Anatomie et de Physiologie, appliquées à la Médecine et à l'Histoire Naturelle |
| Laurent Gerhardt, Compt. rend. | Comptes rendus Mensuels des Travaux Chimiques |
| Lausanne, Bull. Soc. Med. | Bulletin de la Société Médicale de la Suisse Romande |
| Lausanne, Bull. Soc. Vaud. | Bulletin des Séances de la Société Vaudoise des Sciences Naturelles |
| Lausitz. Monatschr. | Lausitzische (und neue Lausitzische) Monatschrift Organ der Oberlausitzischen Gesellschaft der Wissenschaften |
| Leather | Leather |
| Leather Mfr. | Leather Manufacturer |
| Leather Tr. Rev. | Leather Trades Review |
| Leather World | Leather World, The |
| Lederind. | Lederindustrie (Deutsche Gerber-Zeitung) |
| Ledermarkt | Ledermarkt, Der. (See also Collegium) |
| Leeds, Trans. Phil. Soc. | Transactions of the Philosophical and Literary Society of Leeds |
| Leicester, Lit. Phil. Soc. Selection | Selection of Papers of the Literary and Philosophical Society of Leicester |
| Leicester Soc. Rep. | Leicester Literary and Philosophical Society... Report of the Council |
| Leicester Soc. Trans. | Transactions of the Leicester Literary and Philosophical Society |

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| Leide | See Leyden |
| Leiden, Ann. Acad. | Annales Academiæ Lugduno-Batavae |
| Leiden, Tijdschr. Entom. | Tijdschrift voor Entomologie |
| Leipzig, Abh. Jablon. Ges. | Abhandlungen bei Begründung der k. Sächsischen Gesellschaft der Wissenschaften am Tage der zweihundertjährigen Geburtsfeier Leibnizens |
| Leipzig, Abh. Math. Phys. | Abhandlungen der Mathematisch-Physischen Classe der Königlich Sächsischen Gesellschaft der Wissenschaften |
| Leipzig, Arbeit. Physiol. Anst. | Arbeiten aus der physiologischen Anstalt zu Leipzig |
| Leipzig, Astron. Ges. Viertelj. | Vierteljahrsschrift der Astronomischen Gesellschaft |
| Leipzig, Ber. Math. Phys. | Berichte über die Verhandlungen (Math. Phys. Classe) der Königlich Sächsischen Gesellschaft der Wissenschaften zu Leipzig |
| Leipz. Färb. Ztg. | Leipziger Färber- und Zeugdrucker-Zeitung |
| Leipzig Jablon. Preisschr. | Preisschriften gekrönt und herausgegeben von der fürstlich Jablonowski'schen Gesellschaft zu Leipzig |
| Leipzig, Monatschr. Text. Ind. | Leipziger Monatsschrift für Textil Industrie |
| Leipzig, Naturf. Ges. Sitzber. | Sitzungsberichte der Naturforschenden Gesellschaft zu Leipzig |
| Leipzig, Physiol. Anst. Arb. | Arbeiten aus der Physiologischen Anstalt zu Leipzig |
| Leipzig, Schr. Naturf. Ges. | Schriften der Naturforschenden Gesellschaft zu Leipzig |
| Leipzig, Verh. Med. Ges. | Verhandlungen der Medicinischen Gesellschaft |
| Leyden Mus. Notes. | Notes from the Leyden Museum |
| Leo, Mag. | Magazin für Heilkunde und Naturwissenschaft in Pohlen |
| Leoben, Berg. u. Hütt. Jahr. | Berg- und Hüttenmannisches Jahrbuch der k. k. Montan. Lehranstalten zu Leoben und Pribram |
| Leonhard Bronn | See Neues Jahr. Mineral |
| Leonhard Bronn, Jahr. | Jahrbuch für Mineralogie, Geognosie, Geologie, und Petrefaktenkunde |
| Leonhard Bronn, Neu. Jahr. | Neues Jahrbuch für Mineralogie, Geognosie, Geologie und Petrefaktenkunde |
| Leonhard, Taschenbuch | Taschenbuch für die gesammte Mineralogie |
| Leonhard, Zts. | Zeitschrift für Mineralogie |
| Leopold.-Carol. Deutsch. Akad. Naturf. | See Ac. Nat. Curios. Nova Acta. Leopoldina |
| Leopoldina | Leopoldina. Amtliches Organ der Kaiserlichen Leopoldino-Carolinischen Deutschen Akademie der Naturforscher |
| Letters on Brewing | Letters on Brewing |
| Les Modes | Revue hebdomadaire des Sciences et de leurs application |
| Licht. | Licht: Zeitschrift für Photographie: herausgegeben vom Photographischen Verein. zur Berlin |
| Liege, Ann. Acad. | Annales Academiæ Leodiensis |
| Liege Assoc. Ingen. Annu. | See Rev. Univ. Mines |
| Liege, Mem. Soc. Emul. | Memoires de la Société Libre d'Émulation de Liege |
| Liege, Mem. Soc. Sci. | Memoires de la Société (Royale) des Sciences de l'Agriculture, et des Arts a Liege |
| Liege Lab. Fredericq Trav. | Universite de Liege. Institut de Physiologie. Travaux du Laboratoire de Leon Fredericq |
| Lille Inst. Zool. Trav. | Travaux de l'Institut Zoologique de Lille et du Laboratoire de Zoologie Maritime de Wimereux (Pas-de-Calais). Travaux de la Station Zoologique de Wimereux |

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| Lille Mem. Soc. | Memoires de la Société (Imperiale) des Sciences, de l'Agriculture et des Arts de Lille |
| Lille, Mem. Soc. Sci. | Memoires de la Société (Royale) des Sciences, etc., a Lille |
| Lille, Seances Publ. | Seances Publiques de la Société des Amateurs |
| Lille, Tray. | Recueil des Travaux de la Société d'Amateurs des Sciences, de l'Agriculture, et des Arts a Lille |
| Lille, Trav. Mem. | Travaux et Memoires de l'Université de Lille |
| Lima, Mem. Cien. Nat. | Memorias de Ciencias Naturales y de Industrial (Lima) |
| Limbourg, Soc. Sci. Bull. | Bulletin de la Société Scientifique et Litteraire du Limbourg |
| Limoges, Assises | Assises scientifiques de Limoges (Institut des Provinces de France) |
| Lindblom, Bot. Notiser | Botaniska Notiser |
| Linn | Linnaea: ein Journal für die Botanik |
| Linn Entom. | Linnaea Entomologica |
| Linn. Soc. J. | The Journal of the Linnean Society. Botany and Zoology |
| Linn. Soc. Trans. | The Transactions of the Linnean Society of London |
| Linn. Soc. Proc. | Proceedings of the Linnean Society of London |
| Linneska Samf. Handl. | Linneska Samfundets Handlingar for år 1832 |
| Linz, Ber. | Bericht über das Museum Francisco-Carolum in Linz |
| Lisboa, Acad. Sci. Mem. | Historia e Memorias da Academia Real das Sciencias de Lisboa |
| Lisboa, Actas | Actas das Sessoes da Academia Real das Sciencias de Lisboa |
| Lisboa, Ann. | Annaes das Sciencias e Lettras |
| Lisboa, J. Math. Sci. | Jornal de Sciencias Mathematicas, Physicas e Naturaes publicado sob os Auspicios da Academia Real das Sciencias de Lisboa |
| Litterar. Annal. | Litterarische Annalen der gesammten Heilkunde |
| Liverpool Biol. Soc. Proc. | Proceedings and Transactions of the Liverpool Biological Society |
| Liverpool, Lit. Phil. Soc. Proc. | Proceedings of the Literary and Philosophical Society of Liverpool |
| Liverpool Mar. Biol. Comm. | See Liverpool Biol. Soc. Proc.; Liverpool Biol. Soc. Proc. & Trans.; Liverpool Lit. Phil. Soc. Proc. |
| Liverpool Med. Chir. J. | Liverpool Medico-Chirurgical Journal |
| Liverpool School Trop. Med. Mem. | Liverpool School of Tropical Medicine. Memoirs |
| Liverpool, Thompson Yates Lab. Rep. | The Thompson Yates Laboratories Report |
| Loc. Gov. Bd. Rep. (Med. Off.) | ... Annual Report of the Local Government Board. Supplement containing the Reports of the Medical Officer |
| London | See Int. Congr. Hyg. Trans., 1891; Int. Congr. Zool. Proc. 1898 |
| London, Ann. Med. Surg. | Annals of Medicine and Surgery, Records of the occurring Improvements, &c. |
| London, Cryst. Soc. Proc. | Proceedings of the Crystallogical Society |
| London Elec. Soc. Proc. | Proceedings of the London Electrical Society |
| London, Fed. Inst. Brewing J. | Journal of the Federated Institutes of Brewing containing the Transactions of the various Institutes |
| London J. Med. | London Journal of Medicine |
| London, Med. Phys. J. | The Medical and Physical Journal |
| London, Med. Soc. Trans. | Transactions of the Medical Society of London |

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| London, Obstet. Soc. Trans. | Transactions of the Obstetrical Society of London |
| London, Odont. Soc. Trans. | Transactions of the Odontological Society of London |
| London Path. Soc. Trans. | Transactions of the Pathological Society of London |
| Lond. Phot. Soc. | London Photographic Society |
| London Phys. Soc. Proc. | Proceedings of the Physical Society of London |
| London Physiol. J. | London Physiological Journal |
| London Poly. Rev. | The London Polytechnic Review and Magazine |
| London, Poly. Mag. | Polytechnic Magazine and Journal of Science, Letters, and Fine Arts |
| London, Sci. Soc. Proc. | Proceedings of the Scientific Society of London |
| London, Soc. Imp. Med. Trans. | Transactions of the Society for the Improvement of Medical and Chirurgical Knowledge |
| Lotos | Lotos, Jahrbuch für Naturwissenschaft im Auftrage der Vereines "Lotos" |
| Lousiana Planter | Louisiana Planter and Sugar Manufacturer, The |
| Louvaine, Ann. Acad. | Annales Academiae Lovaniensis |
| Lowell Obs. Ann. | Annals of the Lowell Observatory |
| Lucca, Atti Accad. | Atti della R. Accademia Lucchese di Scienze, Lettere, et Arti |
| Lumière | La Lumière; Revue de la Photographie |
| Lumière elec. | Lumière électrique, La |
| Lund, Acta Univ. | Acta Universitatis Lundensis. Lunds Iniversitets Ars-skrift. Afdelningen för Mathematik och Naturvetenskap |
| Lund Bot. För. | See Bot. Centrbl.; Bot. Notiser |
| Lund, Phys. Sällsk. Tidskr. | Physiografiska Sällskapets Tidskrift |
| Lüneb., Denkschr. | Denkschriften des naturwissenschaftlichen Vereins für das Fürstenthum Lüneburg |
| Lüneb., Jahr. Naturwiss. Ver. | Jahresbericht über die Thätigkeit des naturwissenschaftlichen Vereins in Lüneburg |
| Lüneb. Jheft. Naturwiss. Ver. | Jahreshelte des Naturwissenschaftlichen Vereins für das Fürstenthum Lüneburg |
| Luxémb., Inst. Roy. Publ. | Publications de l'Institut Royal Grand-Ducal de Luxembourg: Section des Sciences Naturelles |
| Luxemb. P. | Luxembourg Patent |
| Luxemb. Soc. Bot. Rec. Mem. Trav. | Recueil de Memoires et des Travaux publies par la Société Botanique du Grant-Duche de Luxembourg |
| Luxemb. Soc. Sci. Natur. | Société des Sciences Naturelles du Grand-Duche de Luxembourg |
| Lyon | Lyon scientifique et industriel |
| Lyon, Acad. Sci. Mem. | Memoires de l'Academie des Sciences, Belles-Lettres, et Arts de Lyon |
| Lyon Mus. Hist. Natur. Archiv. | Archives du Museum d'Histoire naturelle de Lyon |
| Lyon Soc. Agric. Ann. | Annales de la Société d'Agriculture, Histoire naturelle et Arts utiles de Lyon. Annales de la Société d'Agriculture, Sciences et Industrie de Lyon |
| Lyon Soc. Bot. Ann. | Annales de la Société Botanique de Lyon |
| Lyon, Soc. Linn. Ann. | Annales de Société Linneenne de la Lyon |
| Lyon, Soc. Linn. Compt. rend. | Comptes Rendus des Travaux de la Société de Médecine |
| Lyon, Soc. Sci. Med. Mem. | Mempires et Comptes-Rendus de la Société des Sciences Medicales de Lyon |
| Lyon Univ. Ann. | Annales de l'Universite de Lyon |
| Maandbl. Natuurweten. | Maandblad voor Natuurwetenschappen, uitgegeven door de Sectie voor Natuurwetenschappen van het Genootschap ter Bevordering van Natuur-, Genees- en Heelkunde te Amsterdam |

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| Maclurian Lyceum, Contrib. | Contributions of the Maclurian Lyceum to the Arts and Sciences |
| Macon Acad. Ann. | Annales de l'Académie de Macon. Société des Arts, Sciences, Belles-Lettres et (d')Agriculture (de Saone-et-Loire) |
| Macon, Spc. Agric. Compt. rend. | Comptes Rendus des Travaux de la Société d'Agriculture, Sciences, et Belles-Lettres |
| Macon Soc. Compt. rend. | Compte Rendu des Travaux de la Société (d'Agriculture), des Sciences, Arts et Belles-lettres, de Macon |
| Madras J. | The Madras Journal of Literature and Science |
| Madras Quart. J. | Madras Quarterly Journal of Medical Science |
| Madrid | See Congr. Int. Hig. Act. 1898 |
| Madrid Acad. Cien. Mem. | Memoires de la Real Academia de Ciencias Exactas, Físicas y Naturales de Madrid |
| Madrid, Anales Hist. Natur. | Anales de Historia Natural |
| Madrid, Anales Minas | Anales de Minas |
| Madrid, Anuar. | Anuario del Real Observatorio de Madrid |
| Madrid, Bol. | Boletín Oficial del Ministerio de Comercio |
| Madrid, Ingen. Ind. Anales | Anales de la Asociación de Ingenieros Industriales |
| Madrid, Mem. | Memorias de la Real Academia de Ciencias |
| Madrid, Revista | Revista de los Progresos de las Ciencias exactas, físicas, y naturales |
| Madrid, Soc. Hist. Natur. Anales | Anales de la Sociedad Española de Historia Natural |
| Mag. Gesammt. Thierheilk. | Magazin für die gesammte Thierheilkunde |
| Mag. Natur. Hist. | The Magazine of Natural History, and Journal of Zoology, Botany, Mineralogy, Geology, and Meteorology |
| Mag. Natur. Phil. | The Magazine of Natural Philosophy |
| Mag. Naturvid. | Magazin for Naturvidenskaberne |
| Mag. Zool. | Magasin de Zoologie |
| Magdeb. V. Ver. Abh. Naturwiss. | Abhandlungen des Naturwissenschaftlichen Vereins zu Magdeburg |
| Magdeb. V. Ver. Festschr. Naturwiss. | Festschrift zur Feier des 25 jährigen Stiftungstages des Naturwissenschaftlichen Vereins zu Magdeburg |
| Magdeb. V. Ver. Jahr. Abh. Naturwiss. | Jahresbericht und Abhandlungen des naturwissenschaftlichen Vereins in Magdeburg. |
| Magendie, J. Physiol. | Journal de Physiologie, experimentale et pathologique |
| Magyar Akad. Ertes. (Math. Termesz.) | Magyar Akadémiai Értesítő. A matematikai, es Természettudományi osztályok közlönye. (Report of the Hungarian Academy. Communications of the Mathematical and Natural Science Sections) |
| Magyar Bőripar | Magyar Bőripar |
| Magyar Nemzeti Múzeum | See Termr. Füzt. |
| Magyar Term. Tars. | See Term. Közön. |
| Magyar Tud. Akad. Ertes. | A Magyar Tudományos Akadémia Értesítője. (Report of the Hungarian Academy of Science) |
| | Akadémiai Értesítő a Magyar Tud. Akadémia Megbízásából. (Report by the Committee of the Hungarian Academy of Science) |
| Magyar Tud. Akad. Ertek. (Math.) | Ertekezések a Matematikai Tudományok köréből. Kiadja a Magyar Tudományos Akadémia. (Memoirs in the Mathematical Sciences. Published by the Hungarian Academy of Science) |

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| Magyar Tud. Akad. Ertek. (Termt.) | Ertekezések a Természettudományok köréből. Kiadja a Magyar Tudományos Akadémia. (Memoirs in the Natural Sciences. Published by the Hungarian Academy of Science) |
| Magyar Tud. Akad. Évk. | A Magyar Tudományos Akadémia Évkönyvei. (Annals of the Hungarian Academy of Science) |
| Maine Loire Soc. Mem. Acad. | Memoires de la Société Académique de Maine et Loire |
| Majocchi, Ann. Fis. Chim. | Annali di Fisica, Chimica, etc. |
| Malpighia | Malpighia. Rassegna mensuale di Botanica |
| Malta P. | Malta Patent |
| Malvern Field Club Trans. | The Transactions of the Malvern Naturalists' Club |
| Manufact. and Build. | The Manufacturer and Builder |
| Manchester, Engin. Proc. | Proceedings of the Manchester Institution of Engi- neers |
| Manchester, Lit. Phil. Soc. Mem. | Memoirs of the Literary and Philosophical Society of Manchester |
| Manchester, Lit. Phil. Soc. Proc. | Proceedings of the Literary and Philosophical Society of Manchester |
| Manchester Micro. Soc. Trans. | Manchester Microscopical Society. Transactions and Annual Report |
| Manchester, Owens Coll. Biol. Lab. Stud. | Studies from the Biological Laboratories of the Owens College |
| Manchester, Owens Coll. Stud. Biol. | Studies in Biology from the Biological Department of the Owens College |
| Mannheim, Jahr. | Jahresbericht des Mannheimer Vereins für Natur- kunde |
| Mans, Soc. Agric. Bull. | Bulletin de la Société d'Agriculture, etc., de la Sarthe |
| Mans, Soc. Bull. | Bulletin de la Société (Royale) d'Agriculture, Sciences et Arts du Mans |
| Mans, Soc. Roy. Trav. | Analyse des Travaux de la Société (Royale) des Arts du Mans |
| Marburg, Ges. Naturwiss. Schr. | Schriften der Gesellschaft zur Beförderung der gesamten Naturwissenschaften zu Marburg |
| Marianini | See Mem. Fis. Sperim. |
| Marne, Soc. Agric. Compte Annuel | Compte annuel et Sommaire des Travaux de la Société Agricole, etc., du département de la Marne |
| Marne, Soc. Agric. Seance | Seance publique de la Société d'Agriculture, etc., du département de la Marne |
| Marseille, Ann. Sci. | Annales de Sciences et de l'Industrie du midi de la France |
| Marseille Fac. Sci. Ann. | Annales de la Faculté des Sciences de Marseille |
| Marseille Lab. Zool. Mar. Trav. | See Marseille Mus. Ann. |
| Marseille, Mem. Acad. | Memoires publies par l'Académie de Marseille |
| Marseille, Mem. Soc. Emul. | Memoires de la Société d'Émulation de la Provence |
| Marseillé Mus. Ann. | Annales du Musée d'Histoire naturelle de Marseille |
| Maschin.-Constr. | Der praktische Maschinen-Construkteur (W. Uhland) |
| Maschinenb. | Der Maschinenbauer |
| Mass. Bd. Health Report | Annual Report of the State Board of Health, Lunacy and Charity of Massachusetts. Annual Report of the State Board of Health of Massachusetts |
| Mass. Insects Report | Annual Report on the Injurious and Beneficial In- sects of Massachusetts |
| Mass. Med. Soc. Commun. | Massachusetts Medical Society's Communications |
| Mat. grasses | Le Matieres grasses |
| Maurice, Soc. Hist. Natur. Rapp. | Septieme Rapport Annuel sur les Travaux de la Société d'Histoire Naturelle de l'Île Maurice |

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| Mauritius, Meteorol. Soc. Proc. | Proceedings, &c., of the Meteorological Society of Mauritius |
| Mauritius, Meteorol. Soc. Trans. | Transactions of the Meteorological Society of Mauritius |
| Mauritius P. | Mauritius Patent |
| Mauritius Roy. Soc. Trans. | Transactions de la Société Royale des Arts et des Sciences de Maurice |
| Meaux, Bull. Soc. Archeol. | Bulletin de la Société d'Archeologie, Sciences, Lettres et Arts du dept. de Seine et Marne |
| Mechan. Engin. Inst. Proc. | Institution of Mechanical Engineers. Proceedings |
| Meckel, Archiv. | Archiv. für Anatomie und Physiologie |
| Meckel, Deut. Archiv. | Deutsches Archiv. für die Physiologie |
| Med. Assoc. J. | Journal edited for the Provincial Medical and Surgical Association |
| Med. Bot. Soc. Trans. | Transactions of the Medico-Botanical Society of London |
| Med. Chem. Unters. | Medicinish-chemische Untersuchungen aus dem Laboratorium für angewandte Chemie zu Tübingen |
| Med. Chir. Soc. Proc. | Proceedings of the Royal Medical and Chirurgical Society of London |
| Med.-Chir. Trans. | Medico-Chirurgical Transactions |
| Med. Chir. Ztg. | Medicinisch-chirurgische Zeitung |
| Med. Congr. | See Congr. Int. Med. C. R., Congr. Int. Sci. Méd. C. T., Congr. Med. Int. Atti., Int. Med. Congr. Trans., Int. Med. Congr. Verh. |
| Med. Jahr. | Medizinische Jahrbücher, von der K. K. Gesellschaft in Wien |
| Med. Klinik. | Medizinische Klinik |
| Med. naturwiss. Archiv. | Medizinisch-naturwissenschaftliches Archiv. |
| Med. Off. India Sci. Mem. | Scientific Memoirs by Medical Officers of the Army of India |
| Med. Phys. J. | The Medical and Physical Journal |
| Med. Rec. | The Medical Record, N. Y. |
| Med. Times | The Medical Times, London |
| Med. Trans. | Medical Transactions |
| Med. Wochenschr. | Medizinische Wochenschrift |
| Med. Ztg. Russ. | Medicinische Zeitung Russlands |
| Medd. Gronland | Meddelelser om Gronland |
| Medd. K. Vetenskapsakad. Nobel-inst. | Meddelanden från K. Vetenskapsakademiens Nobel-institut |
| Meisner, Ann. | Annalen der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften |
| Meisner, Anzeiger | Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften |
| Melbourne | See Victoria |
| Mem. accad. Lincei | Memorie della r. accademia dei Lincei, Classe di scienze fisiche, matematiche e naturali |
| Mem. Accad. Sci. Torino | Memorie della Reale Accademia delle Scienze di Torino |
| Mem. Chem. Soc. | Memoirs and proceedings of the Chemical Society of London prior to 1848 |
| Mem. Coll. Sci. Eng. Kyoto | Memoirs of the College of Science and Engineering, Kyoto Imperial University |
| Mem. Fis. Sperim. | Memorie di Fisica sperimentale |
| Mem. Imp. Mineral. Soc., Petrograd | Memoirs of the Imperial Mineralogical Society of Petrograd |
| Mem. Lepidopt., St. Petersburg. | Memoires sur les Lepidopteres |

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| Mem. Manch. Lit. Phil. Soc. | Memoirs and Proceedings of the Manchester Literary and Philosophical Society |
| Mem. Med. Milit. | Recueil de Memoires de Medecine, de Chirurgie et de Pharmacie Militaires |
| Mem. poud. salp. | Memorial des poudres et salpêtres |
| Mem. rev. soc. cien. "Antonio Alzate" | Memorias y revista de la sociedad científica "Antonio Alzate" |
| Mem. Soc. Ing. civ. | Memoires et Compte-Rendu des travaux de la Société des Ingenieurs Civils, etc. |
| Mem. Soc. Nat. Kiev. | Memoirs of the Society Nat. Kiev. |
| Mem. Valdarnesi | Memorie Valdarnesi |
| Mende, Soc. Agric. Bull. | Bulletin de la Société d'Agriculture, Industrie, Sciences, et Arts de departement de la Lozere |
| Mende, Soc. Agric. Mem. | Memoires et Analyses des Travaux de la Société d'Agriculture, Commerce, Sciences, et Arts de la ville de Mende, departement de la Lozere |
| Merck's Annu. Rep. | Merck's Annual Report |
| Merck's Archiv. | Merck's Archives, New York |
| Messenger Math. | The Messenger of Mathematics |
| Met. | Metallurgical-Metallurgia |
| Met. Chem. Eng. | Metallurgical and Chemical Engineering |
| Met. ital. | Metallurgia italiana, La |
| Met. Rev. | The Metallurgical Review |
| Metal Ind. | The Metal Industry |
| Metal Tech. | Metal Technik |
| Metall. Ind. Ztg. | Deutsche Metall-Industrie-Zeitung |
| Metallarb. | Der Metallarbeiter |
| Metallurgie | Metallurgie |
| Metaxa, Ann. Med. Chir. | Annali medico-chirurgici. |
| Metz Acad. Mem. | Memoires de l'Academie (Imperiale) de Metz |
| Metz, Assises | Assises scientifiques de Metz (Institut des Provinces de France) |
| Metz, Seance Gen. | Société des Lettres, Sciences, Arts, et Agriculture de Metz |
| Metz Soc. Hist. Natur. Bull. | Bulletin de la Société d'Histoire naturelle de Metz |
| Mex. | Mexican, Mexico, Mexicane |
| Mex. P. | Mexican Patent |
| Mex. Mus. Anales | Anales del Museo Nacional de Mexico |
| Mex. Registro Trim. | Registro trimestre, o Coleccion de Memorias de Historia, Literatura, Ciencias, etc., por una Sociedad de Literatos |
| Mex. Soc. "Alzate" Mem. | Memorias de la Sociedad Cientifica "Antonio Alzate" |
| Mexique Archiv. Comm. Sci. | Archives de la Commission Scientifique du Mexique, publiees sous les auspices du Ministere de l'Instruction Publique |
| Meyer Bros. Drug. | Meyer Brothers Druggist, St. Louis |
| Meyer Jahr., Chem. | R. Meyer's Jahrbuch der Chemie |
| Michigan, Fish Comm. Report | Biennial Report of the State Board of Fish Commissioners. (Contains the Michigan Fish Comm. Bull.) |
| Micro. J. | Quarterly Journal of Microscopical Science |
| Micro. Soc. J. | Journal of the Royal Microscopical Society |
| Micro. Soc. Trans. | Transactions of the Microscopical Society of London |
| Midl. Drug. | Midland Druggist and Pharmaceutical Review |
| Midl. Med. Surg. Rep. | Midland Medical and Surgical Reporter |
| Midl. Quart. J. Med. Sci. | The Midland Quarterly Journal of Medical Sciences |
| Milano, Ann. Scienz. | Annali di Scienze e Lettere |

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| Milano, Atti Ginnas. | Atti dell' I. R. Ginnasio Liceale Convitto Longone in Milano |
| Milano, Atti Ist. Lomb. | Atti dell' I. R. Istituto Lombardo di Scienze, Lettere, ed Arti |
| Milano, Atti Soc. Ital. | Atti della Società Italiana di Scienze Naturali |
| Milano, Cagnola Atti | Atti della Fondazione Scientifica Cagnola dalla sua istituzione in poi. |
| Milano, Giorn. Soc. Incor. | Giornale della Società d'Incoraggiamento delle Scienze, etc., stabilita in Milano |
| Milano, Ist. Lomb. Adunanze | Solenni Adunanze del R. Istituto Lombardo di Scienze e Lettere |
| Milano, Ist. Lomb. Rapporti | Rapporti sui Progressi delle Scienze del R. Istituto Lombardo di Scienze |
| Milano, Ist. Lomb. Rend. | Rendiconti dell' Istituto Lombardo di Scienze e Lettere:—Classe di Scienze matematiche e naturali |
| Milano, Mem. Ist. Lomb. | Memorie dell' I. R. Istituto Lombardo di Scienze, etc. |
| Milano, Mem. Ist. Lomb. Veneto | Memorie dell' I. R. Istituto nel regno Lombardo-Veneto |
| Milch. Zentr. | Milchwirtschaftliches Zentralblatt |
| Milch Ztg. | Milch Zeitung |
| Min. Eng. World | Mining and Engineering World |
| Min. J. | The Mining Journal |
| Min. Rev. | Mining Review, a Monthly Record of Geology |
| Min. Sci. | Mining Science |
| Min. Sci. Press | Mining and Scientific Press |
| Min. Smelt. Mag. | The Mining and Smelting Magazine: a monthly review of Practical Mining, Quarrying, and Metallurgy |
| Min. Soc. J. | See Min. Mag. |
| Mineral. Mag. | The Mineralogical Magazine and Journal of the Mineralogical Society of Great Britain and Ireland |
| Mineral. Mitth. | Mineralogische Mittheilungen |
| Mineral. Petr. Mitth. | (Tschermak's) Mineralogische und Petrographische Mittheilungen |
| Mines and Minerals | Mines and Minerals |
| Minn. Acad. Sci. Bull. | Bulletins of the Minnesota Academy of Natural Sciences |
| Minn. Acad. Sci. Pap. | The Minnesota Academy of Natural Sciences at Minneapolis, Minn. Occasional Papers |
| Minn. Bot. Stud. | Geological and Natural History Survey of Minnesota. Minnesota Botanical Studies |
| Miquel, Bull. | Bulletin des Sciences Physiques, et Naturelles en Neerlande |
| Misc. Ent. | Miscellanea Entomologica |
| Mitau, Quatember | Die Quatember |
| Mitth. Artill. Geniew. | Mittheilungen über Gegenstände des Artillerie- und Genie-wesens |
| Mitth. Böhmen. Archit. Ing. Ver. | Mittheilungen des Architekten- und Ingenieur Vereins im Königreiche Böhmen |
| Mitth. Centralst. Wiss.-tech. Unters. | Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen |
| Mitth. Gewerbever. Nassau | Mittheilungen für den Gewerbeverein für Nassau |
| Mitth. Kais. Gesundhts. | Mittheilungen aus dem Kaiserlichen Gesundheitsamte, Berlin |
| Mitth. Königl. Materialprüfungsamt | Mittheilungen aus dem Königlichen Material prüfungsamt zu Gross Lichterfelde West |
| Mitth. Hannov. Gewerbever. | Mittheilungen des Gewerbevereins für Hannover |

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| Mitth. Lebensm. Hyg. | Mittheilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene veröffentlicht vom Schweizer Gesundheitsamt |
| Mitth. Malerei | Technische Mittheilungen für Malerei |
| Mitth. könig. Prüfungsans. | Mittheilungen aus der königlichen Prüfungsanstalt für Wasser-versorgung und Abwässer beseitigung zu Berlin |
| Mitth. Tech. Gew. Mus. | Mittheilungen aus dem Technischen Gewerbe Museum |
| Mitth. Techn. Versuch-samtes | Mittheilungen des k. k. Technischen Versuchsamtes |
| Mitth. Zool. Sta. Neapel | Mittheilungen aus der zoologischen Station zu Neapel, etc. |
| Mo. Insects Report | Annual Report on the Noxious, Beneficial and other Insects, of the State of Missouri, made to the State Board of Agriculture |
| Mod. Sugar Planter | Model Sugar Planter, The |
| Modena, Accad. Sci. Mem. | Memorie della Regia Accademia di Scienze, Lettere ed Arti di Modena |
| Modena, Annu. Soc. Natur. | Annuario della Societa dei Naturalisti in Modena |
| Modena Atti Soc. Natur. | Atti della Societa dei Naturalisti di Modena |
| Modena, Mem. Soc. Ital. | Memorie di Matematica e di Fisica della Societa Italiana delle Scienze |
| Modena, Relazione | Relazione delle Adunanze della R. Accademia di Scienze, Lettere, ed Arti di Modena, nell' Anno Accademico 1842-43 |
| Moigno, Annu. Cosmos | Annuaire du Cosmos |
| Mois chim. electrochim. | Mois chimique et electrochimique, Le |
| Mois min. met. | Mois minier et metallurgique, Le |
| Mois sci. ind. | Mois scientifique et industriel, Le |
| Moleschott, Unters. | Untersuchungen zur Naturlehre des Menschen und der Thiere |
| Moll, Ann. | Annalen der Berg- und Hüttenkunde |
| Moll, Efemeriden | Efemeriden der Berg- und Hüttenkunde |
| Moll, Jähr. Berg. | Jahrbücher der Berg- und Hüttenkunde |
| Moll, Neue Jahr. | Neue Jahrbücher der Berg- und Hüttenkunde |
| Mon. ceram. verr. | Moniteur de la ceramique de la verrerie et journal du ceramiste et du chauxfournier (reunis) |
| Mon. cord. | Moniteur de la cordonnerie |
| Mon. fils. tiss. | Moniteur des fils et tissus |
| Mon. Ind. | Moniteur Industriel |
| Mon. Ind. Belge | Moniteur Industriel Belge |
| Mon. Pap. | Moniteur Papeterie |
| Mon. Sci. | Moniteur Scientifique (Quesneville) |
| Mon. teint. | Moniteur de la teinture des apprêts et de l'impression des tissus |
| Monats. | Monatshefte für Chemie und verwandte Theile anderer Wissenschaften. Gesammelte Abhandlungen aus den Sitzungsberichten der kaiserlichen Akademie der Wissenschaften |
| Monats. Dermatol. | Monatshefte für praktische Dermatologie |
| Monatsbl. Hannover Gewerbever. | Monatsblatt des Gewerbevereins für Hannover |
| Monatschr. Text.-Ind. | Leipziger Monatsschrift für Textil-Industrie |
| Monatschr. Zahn. | Monatsschrift für Zahnärzte |
| Montevideo Mus. Nac. | Anales del Museo Nacional de Montevideo |
| Anales | |
| Monthly Amer. J. Geol. | The monthly Journal of Geology and Natural Science |
| Monthly Archiv. Med. Sci. | Monthly Archives of the Medical Sciences |

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| Monthly Cons. & Trade Report | The monthly Consular and Trade Reports |
| Montpellier, Acad. Proces-Verb. | Extraits des Proces-Verbaux des Seances de l'Academie des Sciences et Lettres |
| Montpellier, Acad. Sci. Mem. | Academie des Sciences et Lettres de Montpellier |
| Montpellier Inst. Zool. Trav. | Travaux originaux du Laboratoire Zoolique de la Faculte des Sciences de Montpellier et de la Station Maritime de Cette |
| Montpellier, Mem. Acad. Sect. Med. | Memoires de l'Academie des Sciences et Lettres: Section de la Medecine |
| Montpellier, Recueil. Bull. | Recueil des Bulletins publies par la Société Libre des Sciences, etc. |
| Montreal Natur. Hist. Soc. Proc. | See Canad. Rec. Sci. |
| Montreal Pharm. J. | Montreal Pharmaceutical Journal |
| Montsouris | See under Paris |
| Morphol. Arb. | Morphologische Arbeiten |
| Morphol. Jahr. | Morphologisches Jahrbuch |
| Moscou | See Congr. Int. Anthropol. C. R. 1892, Congr. Int. Med. C. R. 1897, Congr. Int. Zool. (C. R.) 1892 |
| Moscou, Comment. Soc. Phys. Med. | Commentationes Societatis Physico-Medicae apud Universitatem Mosquensem institutae |
| Moscou, Soc. Natur. Bull. | Bulletin de la Société Imperiale des Naturalistes |
| Moscou, Soc. Natur. Mem. | Memoires de la Société Imperiale des Naturalistes de Moscou |
| Moscou, Soc. Natur. Nouv. Mem. | Nouveaux Memoires de la Société Imperiale des Naturalistes de Moscou |
| Moscow Soc. Sci. Bull. | Bulletin of the Imperial Society of Lovers of Natural Science, Anthropology and Ethnography, in connection with the Imperial University of Moscow |
| Moscow Univ. Mem. (Natur. Hist.) | Scientific Memoirs of the Imperial University of Moscow. Natural History Section |
| Moscow Univ. Mem. (Phys.-Math.) | Scientific Memoirs of the Imperial University of Moscow. Physico-Mathematical Section |
| Moselle, Bull. Soc. Hist. Natur. | Bulletin de la Société d'Histoire Naturelle du departement de la Moselle |
| Moselle, Trav. Soc. Sci. Med. | Exposé des Travaux de la Société des Sciences Medicales de la Moselle |
| Mov. Pict. World | Moving Picture World |
| Mulder, Archief. | Natuur- en Scheikundig Archief. |
| Mulder, Scheik. Verh. | Scheikundige Verhandelingen en Onderzoekingen |
| Müller, Archiv. | Archiv. für Anatomie, Physiologie, und wissenschaftliche Medicin. |
| München, Akad. Abh. | Abhandlungen der Mathematisch-Physikalischen Classe der königlich Bayerischen Akademie der Wissenschaften |
| München, Akad. Sitzber. | Sitzungsberichte der Mathematisch-Physikalischen Classe der k. B. Akademie der Wissenschaften München |
| München Bot. Ver. | See Bot. Centrbl. |
| München, Bull. Akad. | Bulletin der k. Akademie der Wissenschaften |
| München, Denkschr. | Denkschriften der königl. Bayerischen Akademie der Wissenschaften zu München |
| München, Entom. Ver. Mitth. | Mittheilungen des Münchener Entomologischen Vereins |
| München, Gelehrte Anz. | Gelehrte Anzeigen |

- München Ges. Morphol. Sitzungsberichte der Gesellschaft für Morphologie
Physiol. Sitzber. und Physiologie in München
München, Nat. wiss. Tech. Abhandlungen der naturwissenschaftlich-technischen
Comm. Abh. Commission bei der Königl. Baierischen Akademie
München Phot. Ges. See Wien, Photogr. Correspond.
München, Sitzber. Sitzungsberichte der Königl. Baierischen Akademie
der Wissenschaften zu München
München Thierarzney- Jahresbericht der k. Central-Thierarzney-Schule in
Schule Jahr. München
München Thierärztl. Hoch- Jahresbericht der k. Thierärztlichen Hochschule zu
schule Jahr. München
München, Zts. Archit. Zeitschrift des Bayerischen Architekten- und Ingenieur-
Vereins
Munic. Engin. Municipal Engineer
Munic. J. Engin. Municipal Journal and Engineer
Münster, Abh. Aerzt. Ges. Abhandlungen und Beobachtungen der ärztlichen
Gesellschaft zu Münster
Museum Senckenb. Museum Senckenbergianum
Must. Ztg. Leipziger Färber Zeitung (Färberei Musterzeitung)
N. Brunsw. Natur. Hist. Bulletin of the Natural History Society of New Brun-
Soc. Bull. wick
N. England Bot. Club See Rhodora
N. Engl. Eng. New England Engineer, The
N. England J. Med. New England Journal of Medicine and Surgery.
N. Erf. Erfahr. Neueste Erfindungen und Erfahrungen
N. Hampshire San. Bull. New Hampshire Sanitary Bulletin
N. Haven See Connecticut
N. Idea New Idea (The), Detroit
N. Med. Phys. J. New Medical and Physical Journal
N. Mex. Agric. Coll. Bull. New Mexico Agricultural College. Experiment Sta-
tion. Las Cruces, N. M. Bulletin. New Mexico
College of Agriculture and the Mechanic Arts.
Agricultural Experimental Station Bulletin
N. Orleans Med. Surg. J. New Orleans Medical and Surgical Journal
N. Orleans Proc. Proceedings of the New Orleans Academy of Sciences
N. Russ. Soc. Natur. Mem. Memoirs of the New Russian Society of Naturalists
N. S. Wales, Acclim. Soc. Annual Reports (3, 6, and 7) of the Acclimatisation
Report Society of N. S. W.
N. S. Wales Dept. Mines Annual Report of the Department of Mines (and
Report Agriculture), New South Wales
N. S. Wales, Entom. Soc. The Transactions of the Entomological Society of
Trans. New South Wales
N. S. Wales Linn. Soc. Linnean Society of New South Wales. The Macleay
(Macleay Mem. Vol.) Memorial Volume
N. S. Wales, Linn. Soc. The Proceedings of the Linnean Society of New South
Proc. Wales
N. S. Wales P. New South Wales Patent
N. S. Wales, Phil. Soc. Transactions of the Philosophical Society of New
Trans. South Wales
N. S. Wales, Roy. Soc. J. Journal and Proceedings of the Royal Society of
New South Wales
N. S. Wales, Roy. Soc. Transactions of the Royal Society of New South
Trans. Wales
N. Y. Acad. Ann. Annals of the New York Academy of Sciences, Late
Lyceum of Natural History
N. Y. Acad. Mem. New York Academy of Sciences. Memoirs
N. Y. Acad. Trans. Transactions of the New York Academy of Sciences.
Late Lyceum of Natural History

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| N. Y. Acad. Med. Bull. | Bulletin of the New York Academy of Medicine |
| N. Y. Acad. Med. Trans. | Transactions of the New York Academy of Medicine |
| N. Y. Agric. Soc. Trans. | Transactions of the New York State Agricultural Society |
| N. Y. Bot. Club Bull. | Bulletin of the Torrey Botanical Club |
| N. Y. Entom. Soc. J. | Journal of the New York Entomological Society |
| N. Y. Insects Report | Report on the Noxious, Beneficial and other Insects of the State of New York |
| N. Y. J. Med. | New York Journal of Medicine and the Collateral Sciences |
| N. Y. Linn. Soc. Trans. | Transactions of the Linnæan Society of New York |
| N. Y. Lit. Phil. Soc. Trans. | Transactions of the Literary and Philosophical Society of New York |
| N. Y. Lyceum Ann. | Annals of the Lyceum of Natural History of New York |
| N. Y. Lyceum, Proc. | Proceedings of the Lyceum of Natural History in the City of New York |
| N. Y. Med. J. | New York Medical Journal |
| N. Y. Med. Repos. | Medical Repository of New York |
| N. Y. Med. Soc. Trans. | Transactions of the Medical Society of the State of New York |
| N. Y. Mus. Bull. | University of the State of New York. Bulletin of the New York State Museum |
| N. Y. Mus. Mem. | Memoirs of the New York State Museum |
| N. Zeal. Inst. Trans. | Transactions and Proceedings of the New Zealand Institute |
| N. Zeal. Inst. Min. Engin. Trans. | Transactions of the New Zealand Institute of Mining Engineers |
| N. Zeal. J. Sci. | The New Zealand Journal of Science |
| N. Zeal. P. | New Zealand Patent |
| N. Zeal. Pap. & Rep. | New Zealand Papers and Reports relating to Minerals and Mining |
| Nachr. könig. Ges. | Nachrichten von der königlichen Gesellschaft der Wissenschaften zu Göttingen. (Mathematisch-physikalische Klasse) |
| Nancy, Acad. Stanislas. Mem. | Academie de Stanislas. Memoires de la Société (Royale) des Sciences, etc., de Nancy |
| Nancy Soc. Sci. Bull. | Bulletin de la Société des Sciences de Nancy |
| Nancy Soc. Sci. Mem. | Memoires de la Société (Royale) des Sciences, Lettres, et Arts de Nancy |
| Nancy Soc. Sci. Trav. | Precis analytique des Travaux de la Société (Royale) des Sciences, Arts, et Agriculture de Nancy |
| Nantes J. Med. | Journal de la Section de Medecine de la Société Academique du departement de la Loire Inferieure |
| Nantes, Ann. Soc. Acad. | Annales de la Société Academique de Nantes et du departement de la Loire Inferieure |
| Nantes Soc. Sci. Natur. Bull. | Bulletin de la Société des Sciences naturelles de l'Ouest de la France |
| Napoli Accad. Aspir. Ann. | Annali della Accademia degli aspiranti Naturalisti |
| Napoli Accad. Atti | Atti della Reale Accademia delle Scienze Fisiche e Matematiche |
| Napoli Accad. Pontan. Atti | Atti dell' Accademia Pontaniana |
| Napoli Accad. Sci. Atti | Atti della Reale Accademia della Scienze e Belle Lettere; Sezione della Società R. Borbonica |
| Napoli Accad. Sci. Mem. | Memorie della R. Accademia della Scienze |
| Napoli Giorn. Mat. | See Giornale di Matemat. |
| Napoli, Atti Ist. Incorr. | Atti del Real Istituto d'Incoraggiamento alle Scienze Naturali di Napoli |

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| Napoli Lucifero | Il Lucifero |
| Napoli Mus. | Museo di Letteratura e Filosofia |
| Napoli, Ann. Mus. Zool. | Annuario del Museo Zoologico della R. Università di Napoli |
| Napoli Rend. | Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche. (Sezione della Società Reale di Napoli) |
| Napoli Soc. Natur. Boll. | Bollettino della Società di Naturalisti in Napoli |
| Natl. Assoc. Retail Drug, Notes | The Journal of the National Association of Retail Druggists, Chicago |
| Natl. Disp. | National Dispensary |
| Natl. Drug. | National Druggist |
| Natl. Eclect. Med. Assoc. Quart. | The National Eclectic Medical Association Quarterly, Cincinnati |
| Natl. Glass Budget | National Glass Budget |
| Natl. Inst. Bull. | Bulletin of the Proceedings of the National Institution for the Promotion of Science |
| Natur. Can. | Le Naturaliste Canadien. Bulletin de Recherches, Observations et Decouvertes se rapportant a l'Histoire naturelle du Canada |
| Natur. Sicil. | Il Naturalista Siciliano. Giornale di Scienze Naturali |
| Natural. | The Naturalists' Journal |
| Naturaleza | La Naturaleza. Periodico cientifico de la Sociedad Mexicana de Historia Natural |
| Naturalist (Yorks) | The Naturalist: Journal of the West Riding Consolidated Naturalists' Society |
| Naturaliste | Le Naturaliste |
| Nature | Nature |
| Naturf. | Der Naturforscher |
| Natur. Hist. Review | The Natural History Review and Quarterly Journal of Science |
| Naturhist. Notizen | Naturhistorische und chemisch-technische Notizen nach den neuesten Erfahrungen |
| Naturhist. Tidsskr. | Naturhistorisk Tidsskrift |
| Naturwiss. Umschau Chem. Ztg. | Naturwissenschaftliche Umschau der Chemiker-Zeitung |
| Natuurk Tijdschr. | Natuurkundige Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Nat. Hist., &c., uitg. van wege het Genootschap: "Tot nat en vergenoegen," te Arnhem. |
| Nauche, J. Galvan. | Journal du Galvanisme, de Vaccine, etc. |
| Naval Archit. Trans. | Transactions of the Institution of Naval Architects |
| Naval Sci. | Naval Science: a Quarterly Magazine for promoting the improvement of Naval Architecture, Marine Engineering, Steam Navigation, and Seamanship |
| Neapel Zool. Sta., Fauna & Flora | Fauna und Flora des Golfes von Neapel und der angrenzenden Meeres-Abschnitte herausgegeben von der Zoologischen Station zu Neapel |
| Neapel Zool. Sta. Mitth. | Mittheilungen aus der Zoologischen Station zu Neapel |
| Nebraska Univ. Stud. | University Studies. Published by the University of Nebraska |
| Nederl. Archiv. | See Sclenka |
| Nederl. Archief Natuurk. | Nederlandsch Archief voor Genees-en Natuurkunde |
| Nederl. Bot. Ver. Versl. en Meded. | See Nederl. Kruidd. Arch. |
| Nederl. Dierk. Ver. Tijdschr. | Tijdschrift der Nederlandsche Dierkundige Vereeniging |
| Nederl. Entom. Ver. | See Tijdschr. Ent. |

LIST OF ABBREVIATIONS TO LITERATURE

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| Nederl. Kruidk. Archief. | Nederlandsch Kruidkundig Archief |
| Nederl. Lancet | Nederlandsch Lancet. Tijdschrift aan de praktische Chirurgie, etc. |
| Nederl. Tijdschr. Dierkunde | Nederlandsch Tijdschrift voor de Dierkunde, uitgegeven door het koninklijk Zoologisch Genootschap Natura Artis Magistra te Amsterdam |
| Nederl. Tijdschr. Geneesk. | Nederlandsch Tijdschrift voor Geneeskunde, tevens orgaan der Nederlandsche Maatschappij tot de Bevordering der Geneeskunst |
| Neuchatel Soc. Sci. Bull. | Bulletin de la Société des Sciences Naturelles de Neuchatel |
| Neues Bergmänn J. | Neues bergmännisches Journal |
| Neues Jahr. Min. | Neues Jahrbuch für Mineralogie Geologie und Palaeontologie |
| Neues Lausitz. Mag. | Neues Lausitzisches Magazin; unter Mitwirkung der Oberlausitzischen Gesellschaft der Wissenschaften |
| Neue med.-chir. Ztg. | Neue medicinisch-chirurgische Zeitung |
| Neues Nord. Archiv. | Neues nordisches Archiv für Natur und Arzneikunde, verfasst von einer Gesellschaft nordischer Gelehrten |
| Neue Preuss. Provinz. Blätt. | Neue Preussische Provinzial-Blätter |
| Neu-Vorpommern Mitth. | Mittheilungen aus dem naturwissenschaftlichen Vereins für Neu-Vorpommern und Rügen in Greifswald |
| Newbury Field Club Trans. | Transactions of the Newbury District Field Club |
| Newcastle Chem. Soc. Trans. | Newcastle-upon-Tyne Chemical Society. Transactions |
| Newf. P. | Newfoundland Patent |
| Newman. Entom. | The Entomologist |
| Newport Natur. Hist. Soc. Proc. | Proceedings of the Newport Natural History Society |
| Nicholson J. | Journal of Natural Philosophy, Chemistry, and the Arts |
| Nick. | The Nickelodeon |
| Niederl. Archiv. Zool. | Niederländisches Archiv. für Zoologie |
| Niederöstrerr. Gewerb.-Verh. | Verhandlungen des Niederösterreichischen Gewerbe-Vereins |
| Niederrhein. Ges. Naturk. Sitzber. | Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn |
| Niederrhein. Ges. Organ. | Organ für die gesammte Heilkunde; herausgegeben von der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn |
| Nieuw Archief Wisk. | Nieuw Archief voor Wiskunde |
| Nimes Soc. Sci. Bull. | Bulletin de la Société d'Etude des Sciences Naturelles de Nimes |
| Nor. Amer. Med. Chir. Rev. | The North American Medico-Chirurgica] Review |
| Nor. Eng. Inst. Min. Engin. Trans. | North of England Institute of Mining and Mechanical Engineers. Transactions |
| Nor. Staff. Field Club Rep. | (The) North Staffordshire (Naturalists') Field Club (and Archaeological Society). Annual Report (and Transactions) |
| Nord. Brabant, Handel. prov. Genoots. | Handelingen van het provinciaal Genootschap van Kunsten en Wetenschappen in Nord Brabant |
| Nord France Soc. Linn. Bull. | Bulletin de la Société Linneenne du Nord de la France |
| Nord France Soc. Linn. Mem. | Memoires de la Société Linneenne du Nord de la France |

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| Nord, Mem. Soc. Agric. | See Douai |
| Nord, Soc. Agric. Seance Publ. | Seance Publique de la Société d'Agriculture, Sciences, et Arts, etc., du departement du Nord |
| Nordamerik. Monatsber. | Nordamerikanischer Monatsbericht für Natur- und Heilkunde |
| Norddeut. Landwirth | Der norddeutsche Landwirth |
| Nordisches Archiv. | Nordisches (u. Neues Nordisches) Archiv. für Naturkunde und Arzneiwissenschaft |
| Norf. Norw. Natur. Soc. Trans. | Transactions of the Norfolk and Norwich Naturalists' Society |
| Normandie | See Caen |
| Normandie Soc. Linn. Bull. | Bulletin de la Société Linneenne de Normandie |
| Normandie Soc. Linn. Mem. | Memoires de la Société Linneenne de Normandie |
| Normandie Soc. Linn. Seance Publ. | Seance Publiques de la Société Linneenne de Normandie |
| Norsk Tidsk. Vid. Litt. | Norsk Tidsskrift for Videnskab og Litteratur. |
| Norske Videnskab. Skrift. | Det Kongelige Norske Videnskabersselskabs Skrifter i det 19 de Aarhundrede |
| Northampton Natur. Hist. Soc. J. | Journal of the Northampton(shire) Natural History Society and Field Club |
| Northern J. Med | Northern Journal of Medicine |
| Northumb. Natur. Hist. Soc. Trans. | Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne |
| Northwestern Drug. | Northwestern Druggist (The), Minneapolis |
| Norw. P. | Norwegian Patent |
| Notarisia | Notarisia. Commentarium Phycologicum. La Notarisia. Commentario Ficologico Generale. Parte speciale della Rivista Neptunia |
| Notices of Judgment, U. S. Dept. Agric. | Notices of Judgment, U. S. Department of Agriculture |
| Notiz. Archit. Ver. Niederrhein | Notizblatt des Architekten und Ingenieur Vereins für Niederrhein und Westfalen |
| Notiz. Riga | Notizblatt des technischen Vereins zu Riga |
| Nouv. Ann. Math. | Nouvelles Annales de Mathematiques |
| Nouv. Archiv. Miss. Sci. | Nouvelles Archives des Missions Scientifiques et Litteraires |
| Nouv. remedes | Nouveaux remedes, Paris |
| Nova Acta Acad. Nat. Curios. | Novorum Actorum Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum |
| Nova Scotia Inst. Sci. Proc. & Trans. | (The) Proceedings and Transactions of the Nova Scotian Institute of (Natural) Science |
| Nova Scotia, Trans. Lit. Sci. Soc. | Transactions of the Literary and Scientific Society of Nova Scotia |
| Novitates Zool. | Novitates Zoologicae. A Journal of Zoology in connection with the Tring Museum |
| Nuov. Ann. Sci. Natur. | Nuovi Annali delle Scienze naturali |
| Nuov. Antol. Sci. | Nuova Antologia di Scienze, Lettere (Lettere, Scienze) ed Arti |
| Nuov. Cimento | Il Nuovo Cimento, Giornale di Fisica, di Chimica, e di Storia Naturale |
| Nuov. Giorn. Bot. Ital. | Nuovo Giornale Botanico Italiano (e Bullettino della Società Botanica Italiana) |
| Nuov. Notarisia | La Nuova Notarisia. Rassegna (trimestrale) consacrata allo Studio delle Alghe (e Corollario alla "Sylloge Algarum Omnium") |
| Nürnb. Natur. Ges. Abh. | Abhandlungen der Naturhistorischen Gesellschaft zu Nürnberg |
| Nye Hygaea | Nye Hygaea |

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| Nyt Mag. Naturvid. | Nyt Magazin for Naturvidenskaberne |
| Nyt Tidsskr. Fys. Kem. | Nyt Tidsskrift for Fysik og Kemi |
| Oberhess. Ges. Ber. | Berichte der Oberhessischen Gesellschaft für Naturkunde und Heilkunde in Gießen |
| Ontol. Soc. Trans. | Transactions of the Odontological Society of Great Britain |
| Oesterr. Bot. Zts. | Oesterreichische Botanische Zeitschrift |
| Oesterr. Chem. Ztg. | Oesterreichische Chemiker Zeitung |
| Oesterr. landw. Wochenbl. | Oesterreichisches landwirtschaftliches Wochenblatt |
| Oesterr. Med. Jähr. | Medicinisches Jahrbuch des k. k. Oesterreichischen Staates |
| Oesterr. Med. Wochenschr. | Oesterreichische Medicinische Wochenschrift, als Ergänzungsblatt der medicinischen Jahrbücher |
| Oesterr. Wochenschr. | Oesterreichische Wochenschrift für Wissenschaft, Kunst, und öffentliches Leben |
| Oesterr. Zts. Berg. Hüttenw. | Oesterreichische Zeitschrift für Berg- und Hüttenwesen |
| Oesterr.-ung. Zts. Zuckerind. | Oesterreichisch-ungarische Zeitschrift für Zuckerindustrie und Landwirtschaft |
| Off. Gaz. | Official Gazette, United States Patent Office |
| Offenbach. Ver. Naturk. Ber. | Bericht des Offenbacher Vereins für Naturkunde über seine Thätigkeit |
| Oil Colour J. | Oil and Colourman's Trade Journal |
| Oil, Paint and Drug Rep. | Oil, Paint and Drug Reporter |
| Oise | See Beauvais |
| Oise Mem. Soc. Acad. | Memoires de la Société Academique d'Archeologie, Sciences, et Arts du departement de l'Oise |
| Oken Isis | Isis, oder Encyclopädische Zeitung |
| Omaha Drug. | Omaha Druggist (The), Omaha |
| Omodei Ann. Univ. | Annali Universali di Medicina |
| Ontario Entom. Soc. Rep. | Report of the Entomological Society of Ontario |
| Oporto | See Porto |
| Ophthalm. Bibliothek | Ophthalmologische Bibliothek |
| Ophthalm. Hosp. Reports | Ophthalmic Hospital Reports and Journal of the Royal London Ophthalmic Hospital |
| Ophthalmic Rev. | The Ophthalmic Review: a Quarterly Journal of Ophthalmic Surgery and Science |
| Organ Rübenzuckerind. | Organ des Centralvereins für Rübenzuckerindustrie |
| Orgelb. | Die Orgelbauzeitung |
| Orleans Ann. | Annales de la Société Royale des Sciences, Belles-Lettres, et Arts d'Orleans |
| Orleans, Bull. | Bulletin des Sciences Physiques, Medicales, et d'Agriculture d'Orleans |
| Ornis | Ornis, oder das Neueste und Wichtigste der Vögelkunde, etc. |
| Ornith. Jahr. | Ornithologisches Jahrbuch |
| Ornith. Monatsber. | Ornithologische Monatsberichte |
| Ornithol. | The Ornithologist |
| Ornithol. Ool. | The Ornithologist and Oologist |
| Örsted Tidsskrift | Tidsskrift for Naturvidenskaberne |
| Orvos-Termesz. Ertes. | Orvos-Termeszettudományi Értesítő a Kolozsvári Orvos-Termeszettudományi Tarsulat és az Erdélyi Múzeum-Egylet Termeszettudományi Szakosztályának az. szaküléseiről. (Medical and Natural History Proceedings of the sections of the Klausenburg Medical and Natural History Society and of the Natural History section of the Museum Association of Transylvania) |

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| Osnabrück, Jahr. | Jahresbericht des Naturwissenschaftlichen Vereins zu Osnabrück |
| Ottawa Field-Natur. Club Trans. | Ottawa Field-Naturalists' Club Transactions |
| Ottawa Natur. | The Ottawa Naturalist |
| Ouest France Soc. Sci. Nat. Bull. | See Nantes... |
| Oversigt K. Danske Vidensk. Selsk. Forh. | Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger |
| Pacific Drug. Rev. | Pacific Drug Review, Portland |
| Pacific Pharm. | Pacific Pharmacist |
| Padova, Mem. Acad. | Memorie dell' Accademia di Scienze, Lettere, ed Arti di Padova |
| Padova, Nuovi Saggi | Nuovi Saggi dell' Accademia di Scienze, Lettere, ed Arti di Padova |
| Padova, Rivista Period. | Rivista Periodica dei Lavori della I. R. Accademia di Scienze, Lettere, ed Arti di Padova |
| Padova, Soc. Sci. Atti | Atti della Società Veneto-Trentina di Scienze naturali |
| Padova Soc. Sci. Bull. | Buletino della Società Veneto-Trentina di Scienze Naturali residente in Padova |
| Palermo Accad. Atti | Atti della Reale Accademia di Scienze, Lettere e Belle Arti di Palermo |
| Palermo Circ. Mat. Rend. | Rendiconti del Circolo Matematico di Palermo |
| Palermo, Effemeridi | Effemeridi scientifiche e letterarie per la Sicilia; coi Lavori del R. Istituto d'Incoraggiamento per la Sicilia |
| Palermo, Giorn. Sci. Natur. | Giornale di Scienze naturali ed economiche, pubblicato per Cura della Società di Scienze naturali ed economiche di Palermo |
| Palermo, Mem. Spettrosc. Ital. | Memorie della Società degli Spettroscopisti Italiani |
| Palermo Oss. Bull. Meteorol. | Bullettino Meteorologico del Reale Osservatorio di Palermo |
| Palermo Oss. Ossvz. Meteorol. | R. Osservatorio di Palermo. Stazioni di Valverde Osservazioni meteorologiche |
| Palomba, Raccolta | Raccolta di Lettere, etc., intonno alla Fisica ed alle Matematiche |
| Palyamunkak | Palyamunkak. Termesztud (Prize Essays of the Hungarian Academy) |
| Pander, Beitr. Naturk. | Beiträge zur Naturkunde aus den Ostseeprovinzen Russlands |
| Paper. | Paper |
| Paper-Maker Brit. Trade J. | Paper Maker and British Trade Journal |
| Paper Makers' Monthly J. | Paper Makers' Monthly Journal |
| Paper Making | Paper Making |
| Paper Mill | Paper Mill and Woodpulp News |
| Papers Naval Archit. | Papers on Naval Architecture and other subjects connected with naval science |
| Paper Trade J. | Paper Trade Journal |
| Papier-Fabr. | Papier-Fabrikant, Der |
| Papier Ztg. | Papier Zeitung |
| Papierhandel | Der Papierhandel |
| Papilio | Papilio |
| Papir J. | Papir Journalen |
| Par. P. | Paraguay Patent |
| Para. Mus. Hist. Natur. Bol. | Boletim do Museu Paraense de Historia Natural e Ethnographia |
| Paris, Acad. Med. Bull. | Bulletin de l'Academie de Medecine |

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| Paris, Acad. Med. Mem. | Memoires de l'Academie de Medecine |
| Paris, Acad. Sci. Compt. rend. | Comptes Rendus hebdomadaires des Seances de l'Academie des Sciences |
| Paris, Acad. Sci. Mem. | Memoires de l'Academie des Sciences de l'Institut de France |
| Paris, Ann. Cerc. Med. | Annales du Cercle Medecale |
| Paris, Ann. Conserv. | Annales du Conservatoire des Arts et Metiers |
| Paris, Ann. Ecole Norm. | Annales scientifiques de l'Ecole Normale Superieure |
| Paris, Ann. Ponts Chauss. | Annales des Ponts et Chaussées. Memoires et documents relatifs a l'Art des Constructions et au Service de l'Ingenieur |
| Paris, Ann. Soc. Entom. | Annales de la Société Entomologique de France |
| Paris, Annaes Sci. | Annaes das Sciencias, etc., por huma Sociedade de Portuguezes residentes em Paris |
| Paris, Annu. Med. Chir. Hosp. | Annuaire medico chirurgical des Hopitaux, etc., de Paris |
| Paris, Annu. Soc. Met. | Annuaire de la Société Meteorologique de France |
| Paris, Anthropol. Soc. Bull. | Bulletin de la Société d'Anthropologie de Paris |
| Paris, Anthropol. Soc. Mem. | Memoires de la Société d'Anthropologie de Paris |
| Paris, Bull. Fac. Med. | Bulletins de la Faculté de Medecine de Paris et de la Société etablie dans son sein |
| Paris, Bull. Soc. Aerost. | Bulletin de la Société Aerostatique et Meteorologique de France |
| Paris, Bull. Soc. Sci. Natur. | Bulletin de la Société des Sciences Naturelles de France |
| Paris, Bur. Long. Annu. | Annuaire pour l'An., publie par le Bureau des Longitudes |
| Paris, Caus. Sci. | Causeries Scientifiques de la Société Zoologique de France |
| Paris, Club Alpin Franc. Annu. | Annuaire du Club Alpin Français |
| Paris, Com. Intl. Carte Ciel Bull. | Institut de France. Academie des Sciences. Bulletin du Comité International Permanent pour l'Execution Photographique de la Carte du Ciel |
| Paris Congr. Bot. Act. | Actes du Congres International de Botanique tenu a Paris in aout 1867 |
| Paris Congr. Bot. Compt. rend. | ... Comptes Rendus... Congres International de Botanique et d'Horticulture |
| Paris, Congr. Med. Intl. | Congres Medical International de Paris, 1867 |
| Paris, Ecole Norm. Ann. | Annales Scientifiques de l'Ecole Normale Superieure, publies sous les auspices du Ministre de l'Instruction Publique |
| Paris, Ecole Poly. Corresp. | Correspondance sur l'Ecole Polytechnique, a l'usage des Eleves de cette Ecole |
| Paris, Ecole Poly. J. | Journal de l'Ecole Polytechnique publie par le Conseil d'Instruction de cet Etablissement |
| Paris, Ethnog. Soc. Compt. rend. | Comptes Rendus des Seances de la Société d'Ethnographie Americaine et Orientale |
| Paris, Hautes Etudes Bibl. | Bibliotheque de l'Ecole des Hautes Etudes... Section des Sciences Naturelles |
| Paris, Ingen. Civ. Mem. | Memoires et Compte Rendu des Travaux de la Société des Ingenieurs Civils (de France) |
| Paris, J. Bot. | Journal de Botanique, par une Société de Botanistes |
| Paris, J. Chir. | Journal de Chirurgie |
| Paris, Lab. Histol. Trav. | Ecole Pratique des Hautes Etudes. Laboratoire d'Histologie du College de France. Travaux |
| Paris, Mem. Acad. Med. | Memoires de l'Academie (Royale) de Medecine |
| Paris, Mem. Acad. Sci. | Memoires de l'Academie des Sciences |
| Paris, Mem. Inst. | Memoires de la Classe des Sciences mathematiques |

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| Paris, Mem. Soc. Savants | Memoires des Sociétés Savants et Litteraires de la Republique Francaise |
| Paris, Mem. Savants Etrang. | Memoires presentes par divers Savants a l'Academie des Sciences de l'Inst:tut de France |
| Paris, Mem. Soc. Ethnol. | Memoires de la Société Ethnologique |
| Paris, Mem. Soc. Fac. Med. | Memoires de la Société de la Faculte de Medecine |
| Paris, Mem. Soc. Linn. | Memoires de la Société Linneenne de Paris |
| Paris, Mem. Soc. Med. | Memoires de la Société de Medecine |
| Paris, Mem. Soc. Med. Observ. | Memoires de la Société Medicale d'Observation |
| Paris, Mus. Hist. Natur. Ann. | Annales du Museum d'Histoire Naturelle |
| Paris, Mus. Hist. Natur. Archiv. | Archives du Museum d'Histoire Naturelle |
| Paris, Mus. Hist. Natur. Bull. | Bulletin du Museum d'Histoire Naturelle |
| Paris, Mus. Hist. Natur. Cent. | Centenaire de la Fondation du Museum d'Histoire Naturelle |
| Paris, Mus. Hist. Natur. Mem. | Memoires du Museum d'Histoire Naturelle |
| Paris, Mus. Hist. Natur. Nouv. Ann. | Nouvelles Annales du Museum d'Histoire Naturelle |
| Paris, Mus. Hist. Natur. Nouv. Archiv. | Nouvelles Archives du Museum d'Histoire Naturelle |
| Paris Obs. Ann. | Annales de l'Observatoire de Paris |
| Paris, Obs. Montsouris Annu. | (Ville de Paris.) Annuaire de l'Observatoire (municipal de Paris, dit Observatoire) de Montsouris... |
| Paris, Poids Mes. Proc.-Verb. | Comite International des Poids et Mesures. Procès-Verbaux des Seances |
| Paris, Poids Mes. Trav. Mem. | Travaux et Memoires du Bureau International des Poids et Mesures |
| Paris, Recueil Soc. Med. Observ. | Recueil des travaux de la Société Medicale d'Observation de Paris |
| Paris, Recueil. Trav. Soc. Med. Allemande | Recueil des Travaux lus a la Société Medicale Allemande de Paris |
| Paris, Soc. Acclim. Bull. | Bulletin de la Société Zoologique d'Acclimatation |
| Paris, Soc. Anat. Bull. | Bulletin de la Société Anatomique de Paris |
| Paris, Soc. Anthropol. Bull. | Bulletins de la Société d'Anthropologie de Paris |
| Paris, Soc. Anthropol. Mem. | Memoires de la Société d'Anthropologie de Paris |
| Paris, Soc. Biol. Mem. | Comptes Rendus des Seances et Memoires de la Société de Biologie |
| Paris, Soc. Chir. Bull. | Bulletin de la Société de Chirurgie de Paris |
| Paris, Soc. Chir. Mem. | Memoires de la Société de Chirurgie de Paris |
| Paris, Soc. Entom. Ann. | Annales de la Société Entomologique de France |
| Paris, Soc. Entom. Bull. | Bulletin de la Société Entomologique de France |
| Paris, Soc. Geogr. Bull. | Bulletin de la Société de Geographie |
| Paris, Soc. Geogr. Compt. rend. | Compte Rendu des Seances de la Société de Geographie et de la Commission Centrale |
| Paris, Soc. Hist. Natur. Mem. | Memoires de la Société d'Histoire Naturelle de Paris |
| Paris, Soc. Ing. Civ. Mem. | Memoires et Comptes Rendus des Travaux de la Société des Ingenieurs Civils |
| Paris Soc. Linn. Bull. | Bulletin mensuel de la Société Linneenne de Paris |
| Paris, Soc. Math. Bull. | Bulletin de la Société Mathematique de France |
| Paris, Soc. Med. Emul. Bull. | Bulletins de la Société Medicale d'Emulation |
| Paris, Soc. Med. Emul. Mem. | Memoires de la Société Medicale d'Emulation |
| Paris, Soc. Philom. Bull. | Bulletin des Sciences de la Société Philomathique de Paris |

- Paris, Soc. Philom. Mem. Cent. Memoires publies par la Société Philomathique a l'occasion du Centenaire de sa Fondation, 1788-1888
- Paris, Soc. Philom. Nouv. Bull. Nouveau Bulletin des Sciences de la Société Philomathique de Paris
- Paris, Soc. Philom. Proc. Verb. Extraits des Procès-Verbaux des Séances de la Société Philomathique
- Paris, Soc. Phys. Seances Seances de la Société Française de Physique
- Paris, Soc. Spelcol. Mem. Memoires de la Société de Speleologie
- Paris Tow. Nauk Scisl. Pam. Pamiennik Towarzystwa Nauk Scislych w Paryżu
- Paris, Trav. Soc. Amat. Notice des Travaux de la Société des Amateurs des Sciences physiques et naturelles de Paris
- Parlatore, Giorn. Bot. Giornale Botanico Italiano
- Parma, Giorn. Soc. Med. Chir. Giornale della Società Medico-Chirurgica di Parma
- Passau Ber. Nat. Ver. ... Bericht des Naturhistorischen Vereins in Passau für...
- Passau, Jahr. Naturhist. Ver. Jahresbericht des Naturhistorischen Vereins
- Pathol. Soc. Trans. Transactions of the Pathological Society of London
- Pavia Ist. Bot. Atti Atti dell' Istituto Botanico dell' Università di Pavia.
- Segueito dell' Archivio Triennale del Laboratorio di Botanica Crittogamica
- Pavia Lab. Crittog. Archiv. Archivio del Laboratorio di Botanica Crittogamica, presso la R. Università di Pavia
- Peabody Acad. Mem. Memoirs of the Peabody Academy of Science
- Peabody Acad. Report Sixth Annual Report of the Trustees of the Peabody Academy of Science.
- Penn. Univ. Publ. Publications of the University of Pennsylvania
- Penzance Soc. Trans. Transactions of the Natural History and Antiquarian Society of Penzance
- Perf. Essent. Oil Rec. Perfumery and Essential Oil Record
- Perthsh. Soc. Sci. Trans. & Proc. Transactions and Proceedings of the Perthshire Society of Natural Science
- Peru P. Peruvian Patent
- Pet. Nouv. Entom. Petites Nouvelles Entomologiques
- Petermann, Mitth. Dr. A. Petermann's Mittheilungen aus Justus Perthes' Geographischer Anstalt
- Peters, Zts. Zeitschrift für populäre Mittheilungen aus dem Gebiete der Medicin, Chirurgie, und Pharmacie; in Verbindung mit einem Vereine von Aerzten und Pharmaceuten der Herzogthümer Schleswig und Holstein
- Petroleum Petroleum
- Petroleum Gaz. Petroleum Gazette
- Petroleum Rev. Petroleum Review
- Pflüger, Archiv. Physiol. Archiv. für die gesammte Physiologie des Menschen und der Thiere
- Pharm. Pharmakologie
- Pharm.-Ber. Deut.-Arzbuch. Pharmakopoe-Bericht. Die vegetabilischen Drogen des Deutschen Arzneibuches, 5^{te}. Ausgabe, Caesar & Loretz, Halle
- Pharm. Centr. Pharmaceutisches Central-Blatt
- Pharm. Centralh. Pharmaceutische Centralhalle für Deutschland
- Pharm. Era Pharmaceutical Era
- Pharm. J. The Pharmaceutical Journal (and Transactions)
- Pharm. Post Pharmazeutische Post
- Pharm. Weekblad Pharmazeutische Weekblad
- Pharm. Ztg. Pharmazeutische Zeitung

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| Pharm. Zts. | Pharmazeutische Zeitschrift |
| Pharm. Zts. Russland | Pharmaceutische Zeitschrift für Russland |
| Phil. Mag. | Philosophical Magazine |
| Phil. Stud. | Philosophische Studien |
| Phil. Trans. | Philosophical Transactions of the Royal Society of London |
| Phila. Acad. Natur. Sci. J. | Journal of the Academy of Natural Sciences of Philadelphia |
| Phila., Acad. Natur. Sci. Proc. | Proceedings of the Academy of Natural Sciences of Philadelphia |
| Phila. Amer. Entom. Soc. | See Amer. Entom. Soc. |
| Phila. Coll. Pharm. Journ. | Journal of the Philadelphia College of Pharmacy |
| Phila. Eng. Club | Proceedings of the Engineers' Club of Philadelphia |
| Phila. Entom. News | Entomological News (and Proceedings of the Entomological Section of the Academy of Natural Sciences of Philadelphia) |
| Phila. Entom. Soc. Proc. | Proceedings of the Entomological Society of Philadelphia |
| Phila. Med. Mus. | Philadelphia Medical Museum |
| Phila. Med. Phys. J. | The Philadelphia Medical and Physical Journal |
| Phila. Phot. | The Philadelphia Photographer |
| Philippine J. Sci. | Philippine Journal of Science |
| Phot. Archiv | Photographisches Archiv |
| Phot. Bull. | Anthony's Photographic Bulletin |
| Phot. Chronik. | Photographische Chronik und allgemeine Photographen-Zeitung |
| Phot. J. | Wilhelm Horn's Photographische Journal |
| Phot. Corr. (Korr.) | Photographische Korrespondenz |
| Phot. Mag. | Photographisches Magazine |
| Phot. Mitth. | Photographische Mittheilungen |
| Phot. Monats. | Photographische Monatshefte |
| Phot. News | Photographic News |
| Phot. Rundsch. | Photographische Rundschau und Photographisches Centralblatt |
| Phot. Soc. J. | Journal of the Photographic Society of London |
| Phot. Soc. Trans. | Trans. of the Photographic Society of London |
| Phot. Times | The Photographic Times |
| Phot. Wochenbl. | Photographisches Wochenblatt |
| Phot. World | The Photographic World |
| Phot. Centr. | Photographisches Centralblatt |
| Phot. Ztg. | Deutsche Photographen-Zeitung |
| Phys. Rev. | Physical Review |
| Physikal.-Chem. Zentr. | Physikalisch-chemisches Centralblatt |
| Physikal. Meddel. | Physikalske Meddelelser |
| Physikal. Zts. | Physikalische Zeitschrift |
| Physiol. Russe | Le Physiologiste Russe |
| Physiol. Soc. Proc. | See J. Physiol. |
| Phytologist | The Phytologist: a popular Botanical Miscellany |
| Pisa, Ann. Scuola Norm. | Annali della R. Scuola Normale Superiore di Pisa. Scienze Fisiche e Matematiche |
| Pisa, Ann. Univ. Tosc., Sci. Cosm. | Annali della Università Toscana. Scienze Cosmologiche |
| Pisa, Miscell. Med. Chir. | Miscellanea medico-chirurgico-farmaceutiche raccolte in Pisa |
| Pisa, Nuov. Giorn. | Nuovo Giornale de' Letterati |
| Pisa Soc. Sci. Proc. | Atti della Società Toscana di Scienze Naturali residente in Pisa |

- Pisa Soc. Tosc. Atti (Mem.) Atti della Società Toscana di Scienze Naturali residente in Pisa. Memorie
 Pisa Soc. Tosc. Atti (Proc. Verb.) Arti della Società Toscana di Scienze Naturali residente in Pisa. Processi Verball
 Pistoja, Atti Accad. Atti della R. Accademia Pistoiese di Scienze, Lettere, ed Arti; Memorie di Matematica e Fisica
 Plant World Plant World, The
 Plata Mus. Anales Anales del Museo de La Plata. Materiales para la Historia física y moral del Continente Sud-Americano
 Plata Mus. Revista Revista del Museo de La Plata
 Plön Biol. Sta. Forschungsber. Forschungsberichte aus der Biologischen Station zu Plön
 Plymouth Inst. Trans. Annual Reports and Transactions of the Plymouth Institution and Devon and Cornwall Natural History Society
 Pogg. Ann. Poggendorff's Annalen der Physik und Chemie
 Pogg. Ann. Beibl. Poggendorff's Annalen der Physik und Chemie Beiblätter
 Poligrafo Il Poligrafo: Giornale di Scienze, Lettere, ed Arti
 Polit. Il Politecnico
 Pollichia, Jahr. Jahresbericht der Pollichia, eines naturwissenschaftlichen Vereins der Baierischen Pfalz (der Rheinpfalz)
 Polsk. Tow. Przyrod. Kopenika See Kosmos (Lwow)
 Poly. Centr. Polytechnisches Centralblatt
 Poly. Centralh. Polytechnische Centralhalle
 Poly. Mitth. Polytechnische Mittheilungen
 Poly. Notiz. Polytechnisches Notizblatt
 Polygraph. Centr. Polygraphisches Centralblatt
 Pommer, Zts. Schweizerische Zeitschrift für Natur- und Heilkunde
 Pop. Mag. Anthropol. The Popular Magazine of Anthropology
 Pop. Sci. Mon. Popular Science Monthly
 Popular Sci. Rev. The Popular Science Review: a Quarterly Miscellany of entertaining and instructive articles on Scientific subjects
 Pontif. Univ. Gregor. Pontificia Università Gregoriana. Continuazione del Bullettino Meteorologico dell' Osservatorio del Collegio Romano
 Port. P. Portuguese Patent
 Portland, Soc. Natur. Hist. Proc. Proceedings of the Portland Society of Natural History
 Porto, Ann. Soc. Lit. Annaes da Sociedade Lit. Portuguesa
 Porto Soc. Instruc. Rev. Revista da Sociedade de Instrucao do Porto
 Potsdam Astrophys. Obs. Publ. Publicationen des Astrophysikalischen Observatoriums zu Potsdam
 Pottery Gaz. Pottery Gazette
 Pottery and Glass Pottery and Glass
 Power Power
 Prace Mat.-Fiz. Prace Matematyczno-Fizyczne. (Mathematical and Physical Papers)
 Pract. Drug. Practical Druggist and Pharmaceutical Review of Reviews, New York
 Pract. Mag. The Practical Magazine (London)
 Pract. Mechan. J. The Practical Mechanics Journal
 Practitioner The Practitioner
 Prag, Abh. Pojednani Kral. Ceske Spolecnosti Nauk. Abhandlungen der Königl. Böhmisches Gesellschaft der Wissenschaften

- Prag, Česke Ak. Fr. Jos. Pam. Pomatník na oslavu padesaitkeho panovníckeho jubilea jeho Velicňstva Císare a Krále Frantiska Josefa I. Vydała Ceska Akademie Císare Frantiska Josefa pro Vedy, Slovesnost a Umeni. (Memoira in celebration of the fifty years Jubilee of the reign of H. I. & R. M. Francis Joseph I. Published by the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art)
- Prag, Ceske Akad. Fr. Jos. Rozpr. (Trida 2) Rozpravy Ceske Akademie Císare Frantiska Josefa pro Vedy, Slovesnost a Umeni v Praze. (Trida II.) (Transactions of the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art in Prague. Class II)
- Prag, Fr. Jos. Acad. Sci. Bull. Academie des Sciences de l'Empereur Francois Joseph I. Bulletin International
- Prag, Jahr. Böhm. Mus. Jahrbücher des Böhmischen Museums für Natur- und Länderkunde
- Prag, Jahr. Realschule* Jahresbericht der k. k. Böhmischen Ober-Realschule zu Prag
- Prag, Lotos Abh. Abhandlungen des Deutschen Naturwissenschaftlich-Medicinischen Vereines für Böhmen "Lotos"
- Prag, Monatschr. Mus. Monatsschrift der Gesellschaft des vaterländischen Museums in Böhmen
- Prag, Sitzber. Zpravy o Zasedani (Vestník) Kralovske Ceske Společnosti Nauk. Trida. Mathematicko-Prirodove-decka. Sitzungsberichte der Königl. Böhmischen Gesellschaft der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
- Prag Sternw. Magn. Meteorol. Beob. Magnetische und Meteorologische Beobachtungen an der K. K. Sternwarte zu Prag
- Prag, Verh. Verhandlungen der Gesellschaft des vaterländischen Museums in Böhmen
- Prag, Vierteljahrschr. Vierteljahrschrift für die praktische Heilkunde
- Pressburg, Corresp. Blatt. Correspondenzblatt des Vereins für Naturkunde zu Pressburg
- Pressburg, Verh. Verhandlungen des Vereins für Naturkunde zu Pressburg
- Presse Sci. Presse Scientifique des Deux Mondes
- Preuss. Bot. Ver. Sitzber. See Königsberg Schriften
- Preuss. Geod. Inst. Publ. Publication des Königl. Preuss. Geodätischen Instituts
- Preuss. Geod. Inst. Veröff. Veröffentlichung des Königl. Preussischen Geodätischen Instituts
- Preuss. Landes-Oekon.-Kolleg. Archiv. See Landw. Jbüch.
- Pribram, Bergakad. See Wien, Berg- u. Hüttenm. Jbuch.
- Princeton Mus. Contr. Contributions from the (E. M.) Museum of Geology and Archaeology of Princeton College
- Pringsheim, Jahr. Wiss. Bot. Jahrbücher für Wissenschaftliche Botanik
- Print. Reg. Printers' Register
- Prog. agric. viti. Progres agricole et viticole
- Proc. Amer. Acad. Proceedings of the American Academy of Arts Sciences
- Proc. Amer. Inst. Elec. Eng. Proceedings of the American Institute of Electrical Engineers
- Proc. Amer. Micro. Soc. Proceedings of the American Microscopical Society
- Proc. Amer. Pharm. Assoc. Proceedings of the American Pharmaceutical Association
- Proc. Amer. Phil. Soc. Proceedings of the American Philosophical Society

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| Proc. Amer. Soc. Civil Eng. | Proceedings of the American Society of Civil Engineers |
| Proc. Amer. Soc. Micro. | Proceedings of the American Society of Microscopists |
| Proc. Amer. Soc. Test. Mat. | Proceedings of the American Society for Testing Materials |
| Proc. Amer. Water Works Assoc. | Proceedings of American Water Works Association |
| Proc. Assoc. Off. Agric. Chem. | Proceedings of the Association of Official Agricultural Chemists, Washington |
| Proc. Austral. Inst. Min. Eng. | Proceedings Australian Institute of Mining Engineers |
| Proc. Cambr. Phil. Soc. | Proceedings of the Cambridge Philosophical Society |
| Proc. Chem. Soc. | Proceedings of the Chemical Society* (London) |
| Proc. Eng. Soc. Western Penn. | Proceedings of the Engineers' Society of Western Pennsylvania |
| Proc. Inst. Civil Eng. | Proceedings of the Institution of Civil Engineers |
| Proc. Inst. Mech. Eng. | Proceedings of the Institution of Mechanical Engineers |
| Proc. Natl. Wholesale Drug Assoc. | Proceedings of the National Wholesale Druggists' Association |
| Proc. Physiol. Soc. | Proceedings of the Physiological Society |
| Proc. Roy. Soc. Edinb. | Proceedings of the Royal Society of Edinburgh |
| Proc. Roy. Soc. London | Proceedings of the Royal Society of London |
| Proc. Roy. Soc. Med. | Proceedings of the Royal Society of Medicine |
| Proc. Soc. Exp. Biol. Med. | Proceedings of the Society for Experimental Biology and Medicine |
| Proc. U. S. Naval Inst. | Proceedings of U. S. Naval Institute |
| Progres Med. | Le Progres Medical. Journal de Medecine, de Chirurgie et de Pharmacie |
| Progressive Age | Progressive Age |
| Propagation ind. | La Propagation industrielle. Revue mensuelle illustree des inventions, machines, appareils et procedes de la France, etc. |
| Prov. Med. Assoc. J. | Journal of the Provincial Medical Association |
| Prov. Med. Surg. Assoc. Trans. | Transactions of the Provincial Medical and Surgical Association |
| Psyche | Psyché. Organ of the Cambridge Entomological Club |
| Psychol. Med. J. | Journal of Psychological Medicine |
| Publ. Carnegie Inst. | Publications of the Carnegie Institution of Washington |
| Publ. ind. | Publication industrielle des machines par Armengaud |
| Public Analysts Proc. | Proceedings of the Society of Public Analysts |
| Public Health | Public Health |
| Pulp Paper Mag. Can. | Pulp and Paper Magazine of Canada |
| Pure Products | Pure Products. Scientific Station for Pure Products, New York |
| Puy, Soc. Agric. Ann. | Annales de la Société d'Agriculture, Sciences, etc., du Puy |
| Quart. J. Chem. Soc. | Quarterly Journal of the Chemical Society |
| Quart. J. Dent. Sci. | Quarterly Journal of Dental Science. |
| Quart. J. exp. Physiol. | Quarterly Journal of experimental Physiology |
| Quart. J. Geol. Soc. | Quarterly Journal of the Geological Society |
| Quart. J. Math. | The Quarterly Journal of Pure and Applied Mathematics |
| Quart. J. Micro. Sci. | Quarterly Journal of Microscopical Science |
| Quart. J. Micro. Soc. | Quarterly Journal of the Microscopical Society |
| Quart. J. Sci. | The Journal of Science and the Arts Continued as the Quarterly Journal of Science, Literature, and Arts |

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| Quebec, Lit. Hist. Soc. Trans. | Transactions of the Literary and Historical Society of Quebec |
| Queensl. P. | Queensland Patent |
| Queensl. Annu. Rep. Brit. N. Guinea | Annual Report on British New Guinea |
| Queensl. Natur. Hist. Soc. Trans. | Transactions of the Natural History Society of Queensland |
| Queensl. Mus. Ann. | Annals of the Queensland Museum |
| Queensl. Roy. Soc. Proc. | The Proceedings of the Royal Society of Queensland |
| Quekett Micro. Club J. | Journal of the Quekett Microscopical Club |
| Quetelet, Corresp. Math. | Correspondance Mathematique et Physique |
| Radium | Radium, Le |
| Railroad Eng. J. | The Railroad and Engineering Journal. The American Railroad Journal and Van Nostrand's Engineering Magazine have been consolidated in this publication |
| Ranuzzi, Annuario Geogr. | Annuario geographico Italiano |
| Rass. minerar. | Rassegna mineraria metallurgica e chimica |
| Rauch Staub | Rauch und Staub |
| Rayer, Archiv. | Archives de Medecine comparee |
| Reclam, Kosmos | Kosmos: Zeitschrift für angewandte Naturwissenschaften |
| Records Min. | Records of Mining |
| Recueil Math. (Moscou) | Recueil Mathematique. Publie par la Société Mathematique de Moscou |
| Rec. Trav. Chim. Pays-Bas | Recueil des Travaux Chimiques des Pays-Bas (et de la Belgique) |
| Rec. Zool. Suisse | Recueil Zoologique Suisse, comprenant l'Embryologie, l'Anatomic et l'Histologie comparees, la Physiologie, l'Éthologie, la Classification des Animaux vivants et fossiles |
| Regensburg Bot. Ges. | See Flora |
| Regensburg Bot. Ges. Denkschr. | Denkschriften der Königlich (Bayerischen) Botanischen Gesellschaft zu Regensburg |
| Regensburg, Bot. Ztg. | Botanische Zeitung; herausg. von der k. Baier. Botanischen Gesellschaft zu Regensburg |
| Regensburg, Korresp. Blatt. | Korrespondenz-Blatt des Zoologisch-mineralogischen Vereins in Regensburg |
| Reichert, Archiv. | Archiv für Anatomie, Physiologie, und wissenschaftliche Medizin |
| Reil, Archiv. | Archiv. für die Physiologie |
| Reimann's Ztg. | Reimann's Färberzeitung |
| Reims, Seances Acad. | Seances et Travaux de l'Academie de Reims |
| Rend. soc. chim. ital. Rep. | Rendiconti della società chimica italiana |
| Rep. Anal. Chem. | Repertorium, Repertoire Repertory |
| Rep. Anat. Physiol. | Repertorium der analytischen Chemie... Organ des Vereins Analytischer Chemiker |
| Rep. Chim. | Repertoire generale d'Anatomie et de Physiologie pathologiques et de Clinique chirurgicale |
| Rep. Chim. pure (appl.) | Repertoire generale de Chimie (1901-), G. Jaubert |
| Rep. Pat. Inv. | Repertoire de Chimie pure (et appliquée) (Société Chimique de Paris, 1859-1864) |
| Rep. Math. | The Repertory of Patent Inventions and other discoveries and improvements in arts, manufactures and agriculture |
| | Repertorium der literarischen Arbeiten aus dem Gebiete der reinen und angewandten Mathematik |

LIST OF ABBREVIATIONS TO LITERATURE

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| Rep. Meteorol. | Repertorium für Meteorologie, herausgegeben von der Kaiserlichen Akademie der Wissenschaften |
| Rep. Pharm. | Repertorium für die Pharmacie |
| Rep. Phys. | Repertorium der Physik |
| Rep. Phys.-Tech. | See Carl |
| Rep. Chem. Lab. Amer. Med. Ass. | Reports of the Chemical Laboratory of the American Medical Association, Chicago |
| Rep. Council Pharm. Chem. | Reports of the Council of Pharmacy and Chemistry, American Medical Association, Chicago |
| Rep. H. M. Insp. Expl. | Report of His Majesty's Inspectors of Explosives |
| Rep. N. Y. Bd. Pharm. | Report of the New York State Board of Pharmacy |
| Rev. Anthropol. | Revue d'Anthropologie |
| Rev. Artill. | Revue d'Artillerie |
| Rev. Biol. Nord France | Revue Biologique du Nord de la France |
| Rev. Bot. | Rev. de Botanique. Bulletin mensuel de la Société Française de Botanique |
| Rev. Bryol. | Revue Bryologique. Bulletin bimestriel consacré à l'Etude des Mousses et des Hépatiques |
| Rev. chim. ind. | Revue de chimie industrielle et la revue de physique et de chimie |
| Rev. Cours. Sci. | Revue des Cours Scientifiques de la France et de l'Etranger |
| Rev. deux Mondes | Revue des deux Mondes (Paris) |
| Rev. Entom. | Revue d'Entomologie publiée par la Société Française d'Entomologie |
| Rev. gen. Bot. | Revue générale de Botanique |
| Rev. gen. chim. | Revue générale de chimie pure et appliquée (G. Joubert) |
| Rev. gen. lait | Revue générale du lait |
| Rev. gen. mat. color. | Revue générale de matières colorantes et de leurs applications aux textiles |
| Rev. gen. sci. | Revue générale des sciences pure et appliquée |
| Rev. Hortic. | Revue Horticole, Journal d'Horticulture pratique |
| Rev. hyg. pol. sanitaire | Revue d'hygiène et de police sanitaire |
| Rev. Ind. | Revue Industrielle |
| Rev. Ind. Chim. | Revue des industries chimiques et agricoles |
| Rev. Mag. Zool. | Revue et Magazine de Zoologie, pure et appliquée |
| Rev. Maritime Colon. | Revue Maritime (et Coloniale) |
| Rev. Med. Chir. | Revue Medico-Chirurgicale de Paris |
| Rev. Med. Franc. Etrang. | Revue Médicale Française et Étrangère |
| Rev. Met. | Revue de Metallurgie |
| Rev. Mycol. | Revue Mycologique. Recueil trimestriel illustré consacré à l'Étude des Champignons |
| Rev. phot. | Revue de photographie |
| Rev. Quest. Sci. | Revue des Questions scientifiques publiée par la Société Scientifique de Bruxelles |
| Rev. Sci. | (la) Revue Scientifique (de la France et de l'Etranger. Revue des Cours Scientifiques) |
| Rev. Sci. Natur. | Revue des Sciences Naturelles |
| Rev. Soc. Hyg. Aliment. | Revue de la société scientifique d'Hygiène alimentaire et de l'alimentation rationnelle de l'homme |
| Rev. Suisse Zool. | Revue Suisse de Zoologie (et) Annales (de la Société Zoologique Suisse et) du Musée d'Histoire Naturelle de Genève |
| Rev. Univ. Mines | Revue universelle des Mines, de la Metallurgie, des Travaux Publics, des Sciences et des Arts Appliquée à l'Industrie. Annuaire de l'Association des Ingénieurs sortis de l'Ecole de Liège |

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| Rev. Vit. | Revue Viticulture |
| Rev. Zool. | Revue Zoologique, par la Société Cuvierienne |
| Revista Brazil. | Revista Brasileira, Journal de Ciencias, Letras, e Artes |
| Revista, Chim. pure app. | Revista de chimica pure applicada |
| Revista ind. agric. Tucuman | Revista industrial y agrocola de Tucuman |
| Revista Ligure | Revista Ligure, giornale di Lettere, Scienze, etc. |
| Revista Med. Chile | Revista medica de Chile |
| Revista Med. Cirug. Habana | Revista de Medicina y Cirugia, Habana |
| Revista Minera | Revista Minera, periodico cientifico e industrial |
| Revista redl acad. cien. Madrid | Revista de la real academia de ciencias de Madrid |
| Revista Telegr. | Revista de Telegrafos |
| Revista Trim. Microgr. | Revista Trimestral Micrografica. Organo del Laboratorio Histologico de la Facultad de Medicina de Madrid |
| Rhea | Rhea, Zeitschrift für die gesammte Ornithologie |
| Rheinische Monatsschr. | Rheinische Monatsschrift für praktische Aerzte |
| Rheinl. Westphal. | See Bonn. |
| Rheinl. Westphal. Corresp. | Correspondenzblatt des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens |
| Rheinl. Westphal. Verh. | Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens |
| Rheinl. Westphal.-Sitzber. | Sitzungsbericht des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens |
| Rheinpflz Pollichia Festschr. | Festschrift zur Fünfzigjährigen Stiftungsfeier der Pollichia, Naturwissenschaftlichen Vereines der Rheinpflz |
| Rheinpflz Pollichia Jahr. | Jahresbericht der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpflz |
| Rheinpflz Pollichia Mitth. | Mittheilungen der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpflz |
| Rheinpflz Pollichia Sep.-Auszg. | ...Separat-Ausgabe der Pollichia, des Naturwissenschaftlichen Vereines der Pflz |
| Rhodora | Rhodora, Journal of the New England Botanical Club |
| Riga, Arb. Naturf. Ver. | Arbeiten des Naturforschenden Vereins in Riga |
| Riga, Corresp. Blatt. | Correspondenz-Blatt des Naturforschenden Vereins in Riga |
| Riga, Naturf. Ver. | |
| Rio de Janeiro Archiv. | Archivos da Palestra Scientifica do Rio de Janeiro |
| Rio de Janeiro Archiv. | |
| Rio de Janeiro Mus. Nac. | Archivos do Museu Nacional do Rio de Janeiro |
| Rio de Janeiro Mus. Nac. Revista | Revista do Museu Nacional do Rio de Janeiro... (Seguimento aos Archivos do Museu Nacional) |
| Rio de Janeiro Obs. Annaes | (Annaes do Imperial Observatorio do Rio de Janeiro) |
| Rio de Janeiro Obs. Bol. | Boletim mensal do Observatorio do Rio de Janeiro |
| Rio de Janeiro Obs. Revista | Revista do Observatorio. Publicacao mensal do Imperial Observatorio do Rio de Janeiro |
| Rio, Revista | Revista tri mensal de Historia e Geographis: Journal do Instituto Historico e Geographico Brasileiro |
| Rio, Soc. Vell. Trabal. | Trabalhos da Sociedade Vellosiana (Bibliotheca Guanabarensis) |
| Riv. | Rivista |
| Riv. Bolognese | Rivista Bolognese di Scienze e Lettere |
| Riv. Geogr. Ital. | Rivista Geografica Italiana (e Bolletino della Societa di Studi Geografici e Coloniali in Firenze) |

- Riv. Ital. Sci. Natur. Napoli Rivista Italiana di Scienze Naturali e loro Applicazioni
pubblicata per cura degli Aspiranti Naturalisti
- Riv. Ital. Sci. Natur. Siena Rivista Italiana di Scienze Naturali e Bollettino del
Naturalista Collettore, Allevatore, Coltivatore
- Riv. Mat. Rivista di Matematica
- Riv. Mineral. Crist. Rivista di Mineralogia e Cristallografia Italiana
- Riv. Patol. Veg. Rivista di Patologia Vegetale
- Riv. Sci.-Ind. Rivista Scientifico-Industriale delle principali Scoperte
ed Invenzioni fatte nelle Scienze e nelle Industrie
- Riv. Sper. di Freniatria Rivista Sperimentale di Freniatria e di Medicina
legale...
- Riv. Vit. Ital. Rivista di Viticoltura ed Enologia Italiana...
- Robin, J. Anat. Journal de l'Anatomie et de la Physiologie normales
et pathologiques de l'homme et des animaux
- Rochelle See under Charente-Inf.
- Rochester Acad. Sci. Proc. Proceedings of the Rochester New York Academy of
Science
- Rochester Trans. Elec. Transactions of the National Electric Medical Associa-
tion at its Third Meeting, at Rochester, U. S.
- Med. Assoc.
- Rock Products
- Röhr, Notizen Notizen aus dem Gebiete der practischen Pharmacie
- Rollett See Graz.
- Roma See Congr. Med. Int. Atti, 1894
- Roma, Atti Nuovi Lincei Atti dell' Accademia Pontificia de' Nuovi Lincei
- Roma, Atti Reale Accad. Atti della Reale Accademia dei Lincei
- Roma, Corresp. Sci. Corrispondenza Scientifica in Roma per le avanza-
mento delle Scienze, etc.
- Roma Ist. Bot. Annuario Annuario del R. Istituto Botanico di Roma
- Roma Lab. Anat. Norm. Ricerche fatte nel Laboratorio di Anatomia Normale
della R. Università di Roma
- Ric.
- Roma, Nuovi Lincei Mem. Memorie della Pontificia Accademia dei Nuovi Lincei
- Roma, Oss. Coll. Rom. Mem. Memorie del R. Osservatorio del Collegio Romano
- Mem.
- Roma, R. Accad. Lincei Atti della R. Accademia dei Lincei
- (Roma), Soc. Ital. Mem. Memorie di Mathematica e di Fisica della Società
Italiana delle Scienze
- Roma, Soc. Studi Zool. Boll. Bollettino della Società Romana per gli Studi Zoologici
- Roma, Specola Vaticana Pubblicazioni della Specola Vaticana
- Pubbl.
- Roma, Off. Centr. Meteorol. Annali dell' Ufficio Centrale di Meteorologia Italiana
- Ann.
- Römer, Archiv Bot. Archiv für die Botanik
- Roser Wunderlich, Archiv Archiv für physiologische Heilkunde. Continued as
the Archiv. d. Heilk.
- Rotterdam Nieuwe Verh. Nieuwe Verhandelingen van het Bataafsch Genoot-
schap der Proefondervindelijke Wijsbegeerte
Rotterdam
- Rouen, Bull. Soc. Emul. Bulletins (des travaux) de la Société Libre d'Émula-
tion de Rouen
- Rouen, Soc. Sci. Bull. Bulletin de la Société des Amis des Sciences Naturelles
de Rouen
- Rouen, Trav. Acad. Précis analytique des Travaux de l' Academie des
Sciences, Belles-Lettres, et Arts de Rouen
- Roumanie Inst. Meteorol. Annales de l'Institut Meteorologique de Roumanie
- Ann.
- Roy. Engin. Papers Annalele Institutului Meteorologic al Romaniei
- Papers on subjects connected with the duties of the
Corps of Royal Engineers
- Roy. Inst. J. Journal of the Royal Institution of Great Britain

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| Roy. Inst. Proc. | Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain, with Abstracts of the Discourses delivered at the Evening Meetings |
| Roy. School Naval Archit. Ann. | The annual of the Royal School of Naval Architecture and Marine Engineering |
| Roy. Soc. Proc. | Abstracts of the Papers printed in the Philosophical Transactions of the Royal Society of London, from 1800 to 1854 inclusive. Continued as the Proceedings of the Royal Society of London |
| Rugby, Natur. Hist. Soc. Reports | Reports of the Rugby School Natural History Society |
| Russ. Annu. Geol. Mineral. | Russian Annual of Geology and Mineralogy |
| Russ. Annuaire Mines | Annuaire du Journal des Mines de Russie |
| Russ. Chem. Soc. J. | Journal of the Russian Chemical Society |
| Russ. Geogr. Ges. Denkschr. | Denkschriften der Russischen Geographischen Gesellschaft zu St. Petersburg |
| Russ. J. exp. Landw. | Russisches Journal für experimentelle Landwirtschaft |
| Russ. Jahr. Pharm. | Russisches Jahrbuch der Pharmacie |
| Russ. P. | Russian Patent |
| Russ. Pharm. Zts. | Pharmaceutische Zeitschrift für Russland |
| Russ. Phys.-Chem. Soc. J. | Journal of the Russian Physico-Chemical Society of the Imperial University of St. Petersburg |
| Rust, Mag. | Magazin für die gesammte Heilkunde, etc. |
| S. Africa Chem. Metall. Soc. | The Journal of the Chemical and Metallurgical Society of South Africa |
| S. Africa Chem. Metall. Soc. Proc. | The Proceedings of the Chemical and Metallurgical Society of South Africa |
| S. Africa. Mus. Ann. | Annals of the South African Museum |
| S. Africa. Phil. Soc. Trans. | The Transactions of the South African Philosophical Society |
| S. Austral. P. | South Australian Patent |
| S. Austral. Roy. Soc. Mem. | Memoirs of the Royal Society of South Australia |
| S. Austral. Roy. Soc. Trans. | Transactions and Proceedings and Report of the Royal Society of South Australia |
| S. C. Med. Assoc. Trans. | Transactions of the South Carolina Medical Association |
| S. London Entom. Natur. Hist. Soc. Proc. | (Abstract of) Proceedings of the South London Entomological and Natural History Society |
| S. Wales Inst. Civ. Engin. Proc. | Proceedings of the South Wales Institute of Civil Engineers |
| S. Wales Roy. Inst. Report | The annual report of the Council of the Royal Institution of South Wales, with Appendix of Original Papers on Scientific Subjects |
| Sächs. Ingen. Ver. Mitth. | Mittheilungen des Sächsischen Ingenieur-Vereins; herausg. v. d. Verwaltungsrathe des Vereins |
| Sächs. Meteorol. Inst. Abh. | Abhandlungen des Königl. Sächs. Meteorologischen Institutes |
| Sachs. Thüring. Naturwiss. Ver. | See Zts. Naturwiss. |
| Salem | See Essex Institute |
| San Fernando Obs. Marina An. | Anales del Instituto y Observatorio de Marina de San Fernando |
| Sanitary Record | Sanitary Record and Journal of Municipal Engineering, The |
| Santiago Chile, Univ. Anales | (Republica de Chile.) Anales de la Universidad |
| Sao Paulo, Rev. Mus. Paulista | Revista do Museu Paulista |

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| Saone-et-Loire Soc. Sci. Bull. | Bulletins de la Société des Sciences Naturelles de Saone-et-Loire |
| Saone-et-Loire Soc. Sci. Mem. | Memoires de la Société des Sciences Naturelle de Saone-et-Loire |
| Sarthe, Bull. Soc. Agric. | Bulletin de la Société d'Agriculture, Sciences, etc., de la Sarthe |
| Savoie Acad. Mem. | Memoires de l'Academie des Sciences, Belles-Lettres et Arts de Savoie |
| Savoie Soc. Hist. Natur. Bull. | Bulletins de la Société d'Histoire Naturelle de Savoie |
| Savoie Soc. Hist. Natur. (Compt. rend.) | Société d'Histoire Naturelle de Savoie a Chambéry |
| Schaffhausen | See Schweizer. Entom. Gesell. |
| Scheik. Onderz. | See Utrecht. Scheik. Onderzoek |
| Schemnitz Bergakad. | See Wien, Berg- u. Hüttenm. Jahr. |
| Scherer, J. Chem. | Allgemeines Journal der Chemie |
| Schlesw.-Holst. Naturwiss. Ver. Schr. | Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein |
| Schlömilch, Zts. | Zeitschrift für Mathematik und Physik |
| Schneider, Ann. Staatsarz- neik. | Annalen der gessamnten Staatsarzneikunde |
| School Mines Quart. | School of Mines, Quarterly, The |
| School of Mines, Records | Records of the School of Mines |
| Schrader, J. Bot. | Journal für die Botanik |
| Schröder, Berig. Zeevaart. | Berigten en Verhandelungen over eenige onderwerpen des Zeevaarts |
| Schröder, Verh. Zeevaart. | Verhandelungen en Berigten over eenige onderwerpen der Zeevaart-Kunde |
| Schuh Ind. | Schuh Industrie |
| Schumacher, Jahr. | Jahrbuch, (H. C. Schumacher, (1836-38)) |
| Schwäb. Ges. Denkschr. | Denkschriften der Schwäbischen Gesellschaft der Aerzte und Naturforscher |
| Schwalbe | Ornithologische Section der k. k. Zoologische Botanischen Gesellschaft in Wien. Die Schwalbe. Berichte des Comites für Ornithologische Beobachtungs-Stationen in Oesterreich |
| Schweigger, J. (Schw. J.) | Journal für Chemie und Physik |
| Schweiz. Alpenclub Jahr. | Jahrbuch des Schweizer Alpenclub |
| Schweiz. Bot. Ges. Ber. | Berichte der Schweizerischen Botanischen Gesellschaft |
| Schweiz. Entom. Ges. Mitth. | Mittheilungen der Schweizerischen Entomologischen Gesellschaft |
| Schweiz. Ges. Neue Denkschr. | Neue Denkschriften der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften |
| Schweiz. Ges. Verh. | Verhandlungen der Schweizerischen Gesellschaft für die gesammten Naturwissenschaften |
| Schweiz. Monatsschr. | Schweizerische Monatsschrift für praktische Medizin |
| Schweiz. Naturf. Ges. | See Beitr. Kryptog. Schweiz. |
| Schweizer. Naturf. Ges. Verh. | Verhandlungen der Schweizerischen Naturforschenden Gesellschaft |
| Schweiz. Phot.-Ver. | See Wien, Phot. Correspond. |
| Schweiz. Poly. Zts. | Schweizerische polytechnische Zeitschrift. Unter Mitwirkung des Schweizerischen Polytechnikums, etc. |
| Schweiz. Wochenschr. | Schweizerisch Wochenschrift für Chemie und Pharmacie |
| Schweiz. Zts. Heilk. Sci. | Schweizerische Zeitschrift für Heilkunde Science |
| Sci. Abst. | Science Abstracts. Physics and Electrical Engineering |
| Sci. Amer. | Scientific American |

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| Sci. Amer. Suppl. | Scientific American Supplement |
| Sci. Can. | Scientific Canadian |
| Sci. Ind. Bull. Roure-Bertrand Fils | Scientific et Industrial Bulletin Roure-Bertrand Fils |
| Sci. Proc. Roy. Dublin Soc. | Scientific Proceedings of the Royal Dublin Society |
| Sci. Rev. | The Scientific Review and Journal of the Inventors Institute |
| Sci. Trans. Roy. Dublin Soc. | Scientific Transactions of the Royal Dublin Society |
| Scienz. Ital. Congr. | Nuovo Congresso degli Scienziati Italiani in Venezia; porzione geologica |
| Slater, Ibis | The Ibis, a Magazine of General Ornithology |
| Scott. Arbor. Soc. Trans. | Transactions of the Scottish Arboricultural Society |
| Scott. Geogr. Mag. | The Scottish Geographical Magazine |
| Scott. Meteorol. Soc. J. | Journal of the Scottish Meteorological Society |
| Scott. Microb. Soc. Proc. & Trans. | Proceedings and Transactions of the Scottish Microscopical Society |
| Scott. Natur. | A Magazine of Scottish Natural History (and Journal of the Perthshire Society of Natural Science) |
| Scott. Soc. Arts Trans. | Transactions of the Royal Scottish Society of Arts |
| Seeman, J. Bot. | The Journal of Botany, British and Foreign |
| Seifenfabr. | Seifenfabrikant, Der |
| Seifens. Ztg. | Seifensieder Zeitung und Revue über die Harz, Fett und Oelindustrie |
| Seine (Dep. de la) | Sec (France) Soc. Agr. Mem. |
| Seine, Mem. Soc. Agric. | Memoires d'Agriculture par la Société Agricole de la Seine |
| Seine-et-Oise, Mem. | Memoires de la Société des Sciences Naturelles de Seine et Oise |
| Seism. J. Japan | Seismological Journal of Japan |
| Selenka, Archiv Zool. | Niederländisches Archiv für Zoologie |
| Semi-Ann. Rep. Schimmel & Co. | Semi-Annual Report, Schimmel & Co., Miltitz |
| Senckenberg, Naturf. Ges. Abh. | Abhandlungen herausg. von der Senckenbergischen Naturforschenden Gesellschaft |
| Senckenberg, Naturf. Ges. Ber. | Bericht über die Senckenbergische naturforschende Gesellschaft in Frankfurt am Main |
| Shanghai, J. | Journal of the North-China Branch of the Royal Asiatic Society |
| Shanghai, J. Lit. Soc. | Journal of the Literary and Scientific Society of Shanghai |
| Shoe Lea. Reporter | Shoe and Leather Reporter |
| Shropsh. Soc. Trans. | Transactions of the Shropshire Archaeological and Natural History Society |
| Sicilia, Atti Soc. Acclim. | Atti della Società di Acclimazione e di Agricoltura in Sicilia |
| Sidereal Messenger | The Sidereal Messenger |
| Siebenb. Karpath. - Ver. Jahr. | Jahrbuch des Siebenbürgischen Karpathen-Vereins |
| Siebold, J. Geburtshülfe | Journal für die Geburtshülfe, Frauenzimmer, etc., von Elias von Siebold |
| Siebold Kolliker, Zts. | Zeitschrift für wissenschaftliche Zoologie |
| Siebold, Lucina | Lucina; eine Zeitschrift zur Vervollkommung der Entbindungskunst |
| Siena, Atti Accad. | Atti dell' Accademia delle Scienze di Siena detta de' Fisio-critici |
| Silbermann, Rev. Entom. | Revue Entomologique |

LIST OF ABBREVIATIONS TO LITERATURE

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| Silliman, J. | The American Journal of Science and Arts |
| Singapore Roy. Asiat. Soc. | Journal of the Straits Branch of the Royal Asiatic Society. Singapore |
| J. | |
| Sitzber. kais. Akad. Wiss. | Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien (Mathematisch-naturwissenschaftliche Klasse) Abteilungen I, IIa, IIb, III |
| Wien. | |
| Sitzb. könig. Akad. | Sitzungsberichte der königlichen bayerischen Akademie der Wissenschaften zu München |
| München | |
| Sitzber. könig. Akad. Wiss. | Sitzungsberichte der königlich preussischen Akademie der Wissenschaften zu Berlin |
| Berlin | |
| Sitzber. könig. preuss. Akad. | Sitzungsberichte der königlich preussischen Akademie der Wissenschaften |
| Skand. Archiv Physiol. | Skandinavisches Archiv für Physiologie |
| Skand. Naturf. Förh. | Förhandlingar vid det af Skandinaviska Naturforskare och Läkare hållna Möte i Göteborg |
| | Forhandlingerne ved de Skandinaviske Naturforskere |
| Skand. Naturf. Mod. Förh. | 11te Mode i Kjobenhavn fra den 3die til den 9de Juli, 1873 |
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| Skand. Natur. Möt. Förh. | Förhandlingar vid de Skandinaviska Naturforskarnes Tofte Möte i Stockholm från den 7 till den 14 Juli, 1880 |
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| Skandia | Skandia. Tidskrift för Vetenskap och Konst; utgifven af Svenska Litteratur-Föreningen |
| | See Oesterreich. Botan. Zeitschr. |
| Skofitz | Oesterreichisches Botanisches Wochenblatt |
| Skofitz, Bot. Wochenbl. | Oesterreichische Botanische Zeitschrift |
| Skofitz, Bot. Zts. | Smithsonian Contributions to Knowledge |
| Smithsonian Contrib. | Annals of the Astrophysical Observatory of the Smithsonian Institution |
| Smithsonian Inst. Astrophys. Obs. Ann. | Annual Report of the Bureau of (American) Ethnology to the Secretary of the Smithsonian Institution |
| Smithsonian Inst. Bur. Ethnol. Report | Smithsonian Miscellaneous Collections |
| Smithsonian Misc. Coll. | Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures and Condition of the Institution |
| Smithsonian Report | |
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| Snelling's Phot. J. | Snelling's Photographisches Journal |
| Soc. Bot. Ital. Bull. | See Nuovo Giorn. Bot. Ital. |
| Soc. Broteriana | See Coimbra, Soc. Broter. Biol. |
| Soc. Elvet. Sci. Naturf. Atti | See Schweiz. Naturf. Ges. Verh. |
| Soc. Entom. Ross. Horae | Horae Societatis Entomologicae Rossicae variis sermonibus in Russia usitatis editae |
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| Soc. Franc. Bot. | See Rev. Bot. |
| Soc. Franc. Entom. | See Rev. Ent. |
| Soc. Freniatr. Ital. | See Riv. Sper. di Freniatria |
| Soc. Geogr. Finland | See Fennia |
| Soc. Helvet. Actes. | Actes de la Société Helvétique des Sciences Naturelles |
| Soc. Helvet. Sci. Naturf. Act. | See Schweiz. Natf. Ges. Verh. |
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| Soc. Ital. Antrop. | See Arch. Antropologia |
| Soc. Ital. Fis. | See Nuovo Cimento |
| Soc. Ital. Micro. Boll. | See Acireale, Soc. Ital. Micr. Boll. |
| Soc. Ital. Sci. | See (Roma), Soc. Ital. Mem. |
| Soc. Ital. Sci. Nat. | See Milano, Soc. Ital. |
| Soc. Ligust. Sci. Natur. Geogr. | See Genova, Soc. Ligust. Atti |
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| Soc. Malacol. France | See Ann. Malacol. |

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| Soc. Malacol. Ital. Bull. | See Bul. Malacol. Ital. |
| Soc. Meteorol. Ital. | See Moncalieri Oss. Boll. |
| Soc. Mex. Hist. Natur. | See Naturaleza |
| Soc. Napoli | Societa reale di Napoli. Rendiconto dell' Accademia delle Scienze fisiche e mathematiche |
| Soc. Nat. Sicil. | See Nat. Sicil. |
| Soc. Pharm. Anvers | See J. de Pharm. |
| Soc. Public Analysts | See Analyst |
| Soc. Speleol. | See Spelunca, Paris |
| Soc. Telegr.-Engin. Elect. | See Telegr. Eng. J. |
| Soc. Tosc. Sci. Nat. | See Pisa Soc. Tosc. |
| Soc. Ven.-Trent. Sci. Nat. | See Padova Soc. Sci. |
| Soc. Zool. Suisse Ann. | See Rev. Suisse: Zool. |
| Soc. Zool. Tokyo | See Annot. Zool. Jap. |
| Somerset. Archaeol. Soc. Proc. | Proceedings of the Somersetshire Archaeological and Natural History Society |
| Somerset. Sov. Proc. | Somersetshire Archaeological and Natural History Society's Proceedings |
| Somme (Dep. de la) | See under Amiens |
| Southern Pharm. J. | Southern Pharmaceutical Journal |
| Span. P. | Spanish Patent |
| Spatula | Saptula (The), Boston |
| Spelunca. Paris | Spelunca. Bulletin de la Société de Speleologie |
| Sperimentale | Lo Sperimentale. Giornale Italiano di Scienze Meidche |
| Spettatore Vesuvio | Lo Spettatore del Vesuvio e de' Campi Flegrei |
| Spettrosc. Ital. Mem. | Memorie della Societa degli Spettroscopisti Italiani |
| Spongia, Comm. Med. | Commentarii di Medicina |
| Sprechsaal | Sprechsaal |
| Spregnel, Jahr. | Jahrbücher der Gewächskunde |
| Sprengst. Waffen Mun. | Sprengstoffe, Waffen und Munition |
| St. Andrew's Med. Grad. Assoc. Trans. | Transactions of the St. Andrew's Medical Graduates Association |
| St. Barthol. Hosp. Reports | St. Bartholomew's Hospital Reports |
| St. Etienne, Bull. Soc. Ind. Mineral | Bulletin de la Société de l'Industrie Minerale |
| St. Gallen, Ber. Naturwiss. Ges. | Berichte über die Thätigkeit der St. Gallischen Naturwissenschaftlichen Gesellschaft |
| St. Louis, Bot. Gard. Report | Missouri Botanical Garden Report |
| St. Louis, Trans. Acad. Sci. | The Transactions of the Academy of Science of St. Louis |
| St. Petersb. Acad. Sci. Bull. | Bulletin scientifique publie par l'Academie Imperiale des Sciences de St. Petersburg |
| St. Petersb. Acad. Sci. Compt. rend. | Compte Rendu de l'Academie Imperiale des Sciences de St. Petersburg |
| St. Petersb. Acad. Sci. Mem. | Memoires de l'Academie Imperiale des Sciences de St. Petersburg |
| St. Petersb. Acad. Sci. Nova Acta. | Nova Acta Academiae Scientiarum Imperialis Petropolitanae |
| St. Petersb. Acad. Sci. Recueil | Recueil des Actes des Seances Publiques de l'Academie Imperiale des Sciences de St. Petersburg |
| St. Petersb. Ann. Mines Russ. | Annuaire du Journal des Mines de Russie |
| St. Petersb. Archiv. Sci. Biol. | Archives des Sciences Biologiques publiees par l'Institut Imperial de Medecine Experimentale a St. Petersburg |
| St. Petersb., Congr. Bot. Bull. | Bulletin du Congres International de Botanique et d'Horticulture de St. Petersburg le 6/18, le 8/20 et le 10/22 Mai 1869 |

- St. Petersburg. Inst. Med. See St. Petersburg. Arch. Sci. Biol.
 Exper.
 St. Petersburg. Med. Zts. St. Petersburg. Medicinische Zeitschrift
 St. Petersburg. Med. Wochenschr. St. Petersburg. Medicinische Wochenschrift
 St. Petersburg. Mem. Savants Memoires presentes a l'Academie Imperiale des
 Etrang. Sciences de St. Petersburg par divers Savants
 St. Petersburg. Mineral. Ges. Verhandlungen der Russisch-Kaiserlichen Mineralog-
 Verh. ischen Gesellschaft zu St. Petersburg
 St. Petersburg., Russe Geogr. Memoirs de la Société Imperiale Russe de Geographie
 Mem. (Geogr.) Section de Géographie generale
 St. Petersburg., Russ. Geogr. Bulletins of the Imperial Russian Geographical So-
 Soc. Bull. ciety
 St. Petersburg. Schr. Mineral. Schriften der in St. Petersburg gestifteten Kaiserlich-
 Russischen Gesellschaft für die gesammte Mineralo-
 gie
 St. Petersburg. Verh. Mineral. Verhandlungen der Kaiserlich-Russischen Mineralog-
 Ges. ischen Gesellschaft zu St. Petersburg
 St. Petersburg. Verm. Abh. Vermischte Abhandlungen aus dem Gebiete der
 Heilkunde von einer Gesellschaft pract. Aerzte zu
 St. Petersburg. Additional title in 1835, Medizin-
 isch-praktische Abhandlung von Deutschen in Russ-
 land lebenden Aerzten. Continued as the Neue
 Abhandlung St. Petersburg
 St. Quentin, Ann. Annales Agricoles du departement de l'Aisne, publiees
 par la Société des Sciences, Arts, Belles-Lettres,
 et Agriculture de St. Quentin. Annales Scientifiques,
 Agricoles, et Industrielles du departement de l'Aisne
 (Société Academique de Saint Quentin)
 St. Quentin, Mem. Memoires de la Société des Sciences, Arts, Belles-
 Lettres, et Agriculture de la ville de St. Quentin
 St. Quentin, Seances Publ. Société des Sciences, Arts, Belles-Lettres, et Agricul-
 ture de la ville de St. Quentin: Seances publiques.
 St. Quentin, Travaux Société Academique des Sciences, Arts, Belles-Lettres,
 et Agriculture de St. Quentin (Aisne)
 St. Thomas's Hosp. Reports St. Thomas's Hospital Reports
 Stahl Eisen (Zts.) Stahl und Eisen, Zeitschrift für das deutsche Eisen-
 hüttenwesen
 Stavanger Mus. Aarsber. Stavanger Museums Aarsberetning
 Staz. sper. agrar. ital. Stazioni sperimentali agraria italiana, La
 Steiermark. Geog. Mont. Bericht des Geognostisch-montanistischen Vereins für
 Ver. Ber. Steiermark
 Steiermark Mitth. Mittheilungen des Naturwissenschaftlichen Vereines
 für Steiermark
 Steiermark. Mont. Lehr- Die Steiermarkisch ständische montanistische Lehran-
 anst. Jahr. stalt zu Vordernberg
 Stein, Ann. Annalen der Geburtshülfe überhaupt und der Ent-
 bindungsanstalt zu Marburg insbesondere
 Stettin, Entom. Ztg. Entomologische Zeitung; herausg. v. d. Entomo-
 logischen Vereine zu Stettin
 Steyermark. Zts. Steyermärkische Zeitschrift
 Stirling Field Club Trans Stirling Field Club... Transactions
 Stirling Soc. Trans. Stirling Natural History and Archaeological Society.
 Transactions
 Stockholm, Akad. Handl. Kongliga Svenska Vetenskaps Akademiens Hand-
 lingar
 Stockholm, Bihang Akad. Bihang till Kongl. Svenska Vetenskaps Akademiens
 Handl. Handlingar
 Stockholm Bot. Sällsk. See Bot. Centrbl.

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| Stockholm Entom. För. | See Ent. Tidskr. |
| Stockholm, Horti Bergiani Acta | Acta Horti Bergiani. Meddelanden från Kongl. Svenska Vetenskaps-Akademiens Trädgård Bergielund utgifna af Bergianska Stiftelser |
| Stockholm, Öfversigt | Öfversigt af Kongl. Vetenskaps Akademiens Förbandlingar |
| Stockholm Physiol. Lab. Mitth. | Mittheilungen vom Physiologischen Laboratorium des Carolinischen Medico-Chirurgischen Instituts in Stockholm |
| Stockholm, Svenska Läk. Sällsk. Handl. | Handlingar ved Svenska Läkare-Sällskapet |
| Stockholm, Vet. Akad. Lefnadsteckn. | Lefnadsteckningar öfver Kongl. Svenska Vetenskaps-Akademiens efter år 1854 aflidna Ledamöter |
| Stockholm, Ymer | Ymer. Tidskrift utgifven af Svenska Sällskapet för Antropologi och Geografi |
| Strasbourg Soc. Hist. Natur. Mem. | Memoires de la Société du Museum d'Histoire Naturelle de Strasbourg |
| Strasbourg Soc. Sci. Bull. | Bulletin de la Société des Sciences Naturelles de Strasbourg |
| Strasbourg Soc. Sci. J. | Journal de la Société des Sciences, Agriculture, et Arts, du département du Bas-Rhin |
| Strasbourg Soc. Sci. Mem. | Memoires de la Société des Sciences, Agriculture, et Arts, de Strasbourg |
| Stray Feathers | Stray feathers. A journal of Ornithology for India and its dependencies |
| Stricker | See Medizin. Jahr. |
| Sts. Settl. P. | Straits Settlement Patent |
| Student | The Student and Intellectual Observer of Science, Literature, and Art |
| Sturgeon, Ann. Elect. | Annals of Electricity, Magnetism, and Chemistry, and Guardian of Experimental Science |
| Sturgeon, Ann. Phil. | Annals of Philosophical Discovery and Monthly Reporter of the Progress of Practical Science |
| Sucr. | La sucrerie indigene |
| Sucr. Belge | Sucrerie Belge, La |
| Sucr. ind. colon. | Sucrerie indigene et coloniale, La |
| Suddeut. Apoth. Ztg. | Suddeutsche Apotheker Zeitung |
| Suisse Soc. Zool. Ann. | See Rev. Suisse Zool. |
| Surveyor | Surveyor and Municipal and County Engineer, The |
| Sussex Natur. Hist. Soc. Proc. | See Brighton Nat. Hist. Soc. Proc. |
| Svea | Svea. Tijdskrift för Vetenskap och Konst |
| Svensk farm. Tidskr. | Svensk farmaceutisk Tijdskrift, Stockholm |
| Svensk Kem. Tidskr. | Svensk Kemisk Tijdskrift |
| Svenska Läk. Sällsk. Forh. | Forhandlingar ved Svenska Läkare-Sällskapets Sammankomster |
| Svenska Mosskulturför. | Svenska Mosskulturföreningens |
| Svenska Sällsk. Antrop. & Geogr. | See Stockh., Ymer |
| Swart, Verh. | Verhandelingen en Berigten betrekkelijk het Zeewezen en de Zeewaartkunde |
| Swed. P. | Swedish Patent |
| Swiss P. | Swiss Patent |
| Sydney | See New South Wales |
| Sydney Aust. Mus. Mem. | The Australian Museum, Sydney. Memoirs |
| Sydney, Austral. Mus. Records | Records of the Australian Museum |
| Symons, Meteorol. Mag. | Symon's monthly Meteorological Magazine |
| Tablettes Zool. | Tablettes Zoologiques |

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| Tagbl. Frankf. Naturf. | Tageblatt Frankfurter Naturforscher |
| Taprobanian | The Taprobanian, a Dravidian Journal of Oriental Studies in and around Ceylon, in Natural History, Archaeology, Philology, History |
| Tasmania J. Natur. Sci. | The Tasmanian Journal of Natural Science, Agriculture, Statistics, etc. |
| Tasmania P. | Tasmanian Patent |
| Tasmania, Roy. Soc. Monthly Not. | Monthly Notices of Papers and Proceedings of the Royal Society of Tasmania |
| Tasmania, Roy. Soc. Reports | Reports of the Royal Society of Tasmania |
| Taylor, Sci. Mem. | Scientific Memoirs, selected from the Transactions of Foreign Academies and Learned Societies and from Foreign Journals |
| Tech. Blätter | Technische Blätter. Vierteljahrschrift des Deutschen Polytechnischen Vereins in Böhmen |
| Tech. Chem. Jahr. | Technisch-Chemisches Jahrbuch (Biedermann) |
| Tech. Gemeindebl. | Technisches Gemeindeblatt |
| Technikum | Technikum des Ledermarkts |
| Technol. | Le Technologiste (F. Malepeyre) |
| Technol. Quart. | Technology Quarterly |
| Teign Field Club Proc. | Reports of the Proceedings of the Teign Naturalists' Field Club |
| Tekn. Tidskr. | Teknisk Tidskrift |
| Telegr. Eng. J. | Journal of the Society of Telegraph-Engineers and Electricians |
| Telegr. J. | The Telegraphic Journal and Electrical Review |
| Telegr. Ver. Zts. | Zeitschrift des Deutsch-österreichischen Telegraphen-Vereins |
| Temminck, Verh. | Verhandelingen over de natuurlijke Geschiedenis der Nederlandsche overzeesche bezittingen, door de leden der Natuurkundige Commissie in Oost-Indië en andere schrijvers |
| Termr. Füz. | Termeszetrájsi Füzetek... Kiadja a Magyar Nemzeti Múzeum. (Natural History Magazine... published by the Hungarian National Museum) |
| Termt. Közlön. | Termesztudományi Közlöny... Kiadja a K. M. Termesztudományi Társulat. (Natural Science Papers... Published by the Royal Hungarian Natural Science Society) |
| Terrestrial Magn. | Terrestrial Magnetism (and Atmospheric Electricity). An International Quarterly Journal |
| Texas Acad. Sci. Trans. | Transactions of the Texas Academy of Science |
| Text. Amer. | Textile American |
| Text. Col. | The Textile Colorist |
| Text. Färb. Ztg. | Textil und Färberei-Zeitung |
| Text. Mfr. | The Textile Manufacturer |
| Text. Rec. | The Textile Record |
| Text. World Rec. | Textile World Record |
| Text. Ztg. | Textil Zeitung |
| Textilfreund | Der Textilfreund |
| Teyler's Verh. | Geologische Verhandeling af Antwoord af de in 1828 uitgeschrevene en in 1830 herhaalde Pryspraak: Wat men van Geologie, etc. |
| Therap. Gaz. | The Therapeutic Gazette |
| Therap. Monats. | Therapeutische Monatshefte |
| Therap. Neuheit | Therapeutischen Neuheiten, Leipzig |
| Therapist | Therapist (The) London |

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| Thomson, Ann. Phil. | Annals of Philosophy, or Magazine of Chemistry, Mineralogy, Mechanics, and the Arts |
| Thomson, Archiv. Entom. | Archives Entomologiques |
| Thomson, Rec. | Records of General Science |
| Thonind. Ztg. | Thonindustrie-Zeitung |
| Thronhjelm, Skrifter | Der Kongelige Norske Videnskabers-Selskabs Skrifter i det 19 de Aarhundrede |
| Tidskr. Kemi. Farm. | Tidsskrift for Kemi og Farmaci Terapi |
| Terapi | |
| Tidskr. Mat. | Tidsskrift for Matematik |
| Tidskr. Mat. Fys. | Tidsskrift för Matematik och Fysik, tillegnad den Svenska Elementar-Undervisningen |
| Tidskr. Phys. Chem. | Tidsskrift for Physik og Chemi samt disse Videnskabers Anvendelse |
| Tiedemann, Zts. | Zeitschrift für Physiologie |
| Tijdschr. Entom. | Tijdschrift voor Entomologie; uitgegeven door de Nederlandsche Entomologische Vereeniging |
| Tijdschr. Genootsch. Vis. Unita | Tijdschrift voor Genees-, Heel-, Verlos-, en Scheikundige Wetenschappen, van Wege et Genootschap: "Vis Unita Fortior," te Hoorn. |
| Tijdschr. Ing. | Tijdschrift van het Koninklijk Instituut van Ingenieurs |
| Tijdschr. nijv. | Tijdschrift ter befordering van nijverheid |
| Tijdstroom. | De Tijdstroom; Maandschrift gewijd van Wetenschap, etc. |
| Tilesius, Jahr. | Jahrbuch der Naturgeschichte zur Anzeige und Prüfung |
| Timehri | Timehri being the Journal of the Royal Agricultural and Commercial Society of British Guiana |
| Tirol, Ber. Ver. Durchf. | Bericht über die General-Versammlung des Vereins zur geogr. montan. Durchforschung des Landes Tirol, etc. |
| Tischl. Ztg. | Deutsche Tischlerzeitung |
| Tokio Univ. Mem. | Memoirs of the Science Department, University of Tokio, Japan |
| Tokyo Bot. Soc. | See Bot. Mag., Tokyo |
| Tokyo, Coll. Sci. J. | The Journal of the College of Science, Imperial University, Japan |
| Tokyo Geogr. Soc. J. | Journal of the Tokio Geographical Society |
| Tonind. Ztg. | Tonindustrie Zeitung |
| Töpfer Ztg. | Deutsche Töpfer und Ziegler Zeitung |
| Torino, Accad. Sci. Atti | Atti della R. Accademia delle Scienze di Torino |
| Torino, Accad. Sci. Mem. | Memoire della R. Accademia delle Scienze di Torino |
| Torino, Ann. Clin. | Annali Clinici |
| Torino, Lavori Sci. Fis. Mat. | Notizia storica dei lavori fatti dalla Classe di Scienze Fisiche e Matematiche della R. Accademia delle Scienze negli anni 1864-65 |
| Torino Mus. Boll. | Bollettino dei Musei di Zoologia ed Anatomia comparata della R. Università di Torino |
| Torrey Bot. Club Bull. | Bulletin of the Torrey Botanical Club |
| Torrey Bot. Club Mem. | Memoirs of the Torrey Botanical Club |
| Tortolini, Ann. | Annali di Scienze, Matematiche, e Fisiche |
| Toulouse Acad. Sci. Bull. | Bulletin de l'Académie des Sciences, Inscriptions et Belles-Lettres de Toulouse |
| Toulouse, Acad. Sci. Mem. | Memoires de l'Académie des Sciences, Inscriptions et Belles-Lettres de Toulouse |
| Toulouse Fac. Sci. Ann. | Annales de la Faculté des Sciences de Toulouse, pour les Sciences Mathématiques et les Sciences Physiques |
| Toulouse Obs. Ann. | Annales de l'Observatoire Astronomique, Magnétique et Meteorologique de Toulouse. |

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| Toulouse Soc. Hist. Natur. Bull. | Bulletin de la Société d'Histoire Naturelle de Toulouse |
| Toulouse Soc. Sci. Bull. | Bulletin de la Société des Sciences Physiques et Naturelles de Toulouse |
| Trans. Acad. Sci. St. Louis | Transactions of the Academy of Sciences of St. Louis |
| Trans. Amer. Ceram. Soc. | Transactions of the American Ceramic Society |
| Trans. Amer. Electrochem. Soc. | Transactions of the American Electrochemical Society |
| Trans. Amer. Inst. Chem. Eng. | Transactions of the American Institute of Chemical Engineers |
| Trans. Amer. Inst. Homoeop. | Transactions of the American Institute of Homoeopathy, Philadelphia |
| Trans. Amer. Inst. Min. Eng. | Transactions of the American Institute of Mining Engineers |
| Trans. Amer. Med. Assoc. Sec. Pharm. Therap. | Transactions of the Section on Pharmacology and Therapeutics of the American Medical Association |
| Trans. Amer. Micro. Soc. | Transactions of the American Microscopical Society |
| Trans. Amer. Soc. Civ. Eng. | Transactions of the American Society of Civil Engineers |
| Trans. Cambr. Phil. Soc. | Transactions of the Cambridge Philosophical Society |
| Trans. Can. Inst. | Transactions of the Canadian Institute |
| Trans. Engl. Ceram. Soc. | Transactions of the English Ceramic Society |
| Trans. Faraday Soc. | Transactions of the Faraday Society |
| Trans. Geol. Soc. S. Africa | Transactions of the Geological Society of South Africa |
| Trans. Illum. Eng. Soc. | Transactions of the Illuminating Engineering Society |
| Trans. Inst. Brew. | Transactions of the Institute of Brewing |
| Trans. Jenner Inst. Prev. Med. | Transactions of the Jenner Institute of Preventive Medicine |
| Trans. Kansas Acad. Sci. | Transactions of the Kansas Academy of Science |
| Trans. Med. | Transactions Medicales; Journal de Medecine pratique |
| Trans. Min. Geol. Inst. India | Transactions of the Mining and Geological Institute of India |
| Trans. Natl. Ecler. Med. Assoc. | Transactions National Eclectic Medical Association, Indianapolis |
| Trans. Nova Scotia Inst. Sci. | Transactions of the Nova Scotia Institute of Science |
| Transv. P. | Transvaal Patent |
| Trans. Path. Soc. | Transactions of the Pathological Society |
| Trans. Roy. Irish Acad. | Transactions of the Royal Irish Academy |
| Trans. Roy. Soc. Can. | Transactions of the Royal Society of Canada |
| Trans. Roy. Soc. Edinb. | Transactions of the Royal Society of Edinburgh |
| Trans. Roy. Soc. London | Transactions of the Royal Society of London |
| Trans. Soc. Engin. | Society of Engineers, Transactions |
| Trav. Com. Hyg. Publ. | Recueil des Travaux du Comité consultatif d'Hygiène Publique de France et des Actes Officiels de l'Administration Sanitaire |
| Trenton Natur. Hist. Soc. J. | Journal of the Trenton, New Jersey, Natural History Society |
| Treviso, Mem. Ateneo | Memorie Scientifiche e Letterarie dell' Ateneo di Treviso |
| Trief, Jahr. | Jahresbericht der Gesellschaft für nützliche Forschungen zu Trier |
| Triest Zool. Sta. Arb. | See Wien. Zool. Inst. Arb. |
| Trieste, Boll. | Bollettino della Società Adriatica di Scienze Naturali in Trieste |
| Trieste Mus. Civ. Atti | Atti del Museo Civico di Storia Naturale di Trieste |
| Trieste, Program. Civ. Scuola | Programma della Civica Scuola Reale autonoma in Trieste |

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| Trinidad Field Natur. Club J. | Journal of the Trinidad Field Naturalists' Club |
| Trinidad P. | Trinidad Patent |
| Trinidad, Proc. Sci. Assoc. | Proceedings of the Scientific Association of Trinidad |
| Trinidad, Sci. Assoc. Proc. | Proceedings of the Scientific Association of Trinidad |
| Trommsdorff, J. Pharm. | Journal der Pharmacie für Aerzte und Apotheker, und Chemiker |
| Tromso, Mus. Aarsh. | Tromso Museums Aarshefte |
| Tropenpflanzer | Tropenpflanzer (Der), Berlin |
| Tsch. Mineral. Mitth. | Tschermak's Mineralogische Mittheilungen |
| Tuberculosis | Tuberculosis. The Journal of the National Association for the Prevention of Consumption and other forms of Tuberculosis |
| Tübinger Blätter | Tübinger Blätter für Naturwissenschaften und Arzneikunde |
| Tübingen Bot. Inst. Unters. | Untersuchungen aus dem Botanischen Institut zu Tübingen |
| Tunis P. | Tunis Patent |
| Turin, Mem. Acad. | Memoires de l'Academie Royale des Sciences de Turin |
| Tyneside Natur. Field Club Trans. | Transactions of the Tyneside Naturalist's Field Club |
| U. K. Mar. Biol. Assoc. J. | Journal of the Marine Biological Association of the United Kingdom |
| U. S. Bur. Anim. Ind. Bull. | U. S. Department of Agriculture. Bureau of Animal Industry |
| U. S. Bur. Anim. Ind. Report | Annual Report of the Bureau of Animal Industry |
| U. S. Chief Signal Off. Ann. Report | Annual Report of the Chief Signal Officer (of the Army) to the Secretary of War |
| U. S. Coast Geod. Surv. Bull. | United States Coast and Geodetic Survey. Bulletin |
| U. S. Comm. Agric. Report | Report of the Commissioner of Agriculture |
| U. S. Dept. Agric. Bull. | Bulletins of the Department of Agriculture, U. S. |
| U. S. Dept. Agric. Report | Reports of the Department of Agriculture, U. S. |
| U. S. Dept. Agric. Yearb. | Yearbook of the United States Department of Agriculture |
| U. S. Disp. | United States Dispensatory |
| U. S. Div. Biol. Surv. Bull. | U. S. Department of Agriculture. Division of Biological Survey. Bulletin |
| U. S. Div. Chem. Bull. | U. S. Department of Agriculture. Division of Chemistry. Bulletin |
| U. S. Div. Entom. Bull. | U. S. Department of Agriculture. Division of Entomology |
| U. S. Div. Entom. Insect Life | U. S. Department of Agriculture. Division of Entomology. (Periodical Bulletin.) Insect Life |
| U. S. Div. Entom. Tech. Ser. | U. S. Department of Agriculture. Division of Entomology. Technical Series |
| U. S. Div. Ornith. Mamm. Bull. | U. S. Department of Agriculture. Division of Economic Ornithology and Mammalogy. Bulletin |
| U. S. Div. Soils Bull. | U. S. Department of Agriculture. Division of (Agricultural) Soils. Bulletin |
| U. S. Entom. Comm. Bull. | Department of the Interior... Bulletin of the United States Entomological Commission |
| U. S. Entom. Comm. Report | (U. S.) Department of the Interior (Agriculture)... Report of the United States Entomological Commission |
| U. S. Fish Comm. Bull. | Bulletin of the United States Fish Commission |
| U. S. Fish Comm. Report | United States Commission of Fish and Fisheries. Report of the Commissioner |

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| U. S. Geol. Surv. | United States Geological Survey |
| U. S. Monthly Weath. Rev. | (United States) Monthly Weather Review |
| U. S. Mus. Bull. | Department of the Interior... Bulletin of the United States National Museum |
| U. S. Mus. Proc. | Department of the Interior... Proceedings of the United States National Museum |
| U. S. Mus. Report | See Smithsonian Rep. |
| U. S. Mus. Spec. Bull. | Smithsonian Institution. United States National Museum. Special Bulletin |
| U. S. Naval Inst. Proc. | United States Naval Institute Proceedings |
| U. S. Naval Med. Bull. | United States Naval Medical Bulletin |
| U. S. Naval Obs. Publ. | Publications of the United States Naval Observatory |
| U. S. N. Amer. Fauna | U. S. Department of Agriculture. Division of Ornithology and Mammalogy. North American Fauna |
| U. S. P. | United States Patent |
| U. S. Ph. | United States Pharmacopoeia |
| U. S. Secty. Agric. Report | Report of the secretary of agriculture |
| U. S. Signal Serv. Notes | United States of America: War Department. Signal Service Notes |
| U. S. Signal Serv. Pap. | United States of America, War Department. Professional Papers of the Signal Service |
| U. S. Surv. Terr. Reports | ... Annual Report of the United States Geological (and Geographical) Survey of the Territories |
| U. S. Weath. Bur. Bull. | U. S. Department of Agriculture. Weather Bureau. Bulletin |
| U. S. Weath. Bur. Report | U. S. Department of Agriculture. Weather Bureau. Report of the Chief of the Weather Bureau |
| U. Serv. Inst. J. | Journal of the royal United Service Institution, Whitehall Yard |
| Udine, Relazioni | Relazioni intorno agli Atti dell' Accademia di Udine |
| Uhland's Tech. Rund. | Uhland's Technische Rundschau |
| Umschau | Umschau, Die |
| Ung. Naturwiss. Ver. Jahr. | Abhandlungen aus dem dritten Bande der Jahrbücher des Ungarischen naturwissenschaftlichen Vereins zu Pest, in Deutscher Uebersetzung Red. von J. Szabo |
| Univ. Ill. Bull. | University of Illinois Bulletin |
| Unters. Naturlehre | Untersuchungen zur Naturlehre des Menschen und der Thiere |
| Upsala, Arsskrift | Universitets Arsskrift utgifven af Kongl. Vetenskaps-Societeten i Upsala |
| Upsala Bot. För. | See Bot. Notiser |
| Upsala, Diss. Acad. | Dissertationes Academicæ Upsaliæ habitæ |
| Upsala, Frey Tidskr. | Frey Tidskrift för Vetenskap och Konst |
| Upsala Läkareför. Förh. | Upsala Läkareförenings Förhandlingar |
| Upsala Naturvet. Student-sällsk. | See Bot. Centrbl. |
| Upsala, Soc. Sci. Nova Acta | Nova Acta Regiæ Societatis Scientiarum Upsaliensis |
| Urug. P. | Uruguay Patent |
| Utrecht, Aanteek. Prov. Genoots. | Aanteekeningen van het Verhandelde in de Sectie-Vergaderingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen |
| Utrecht, Ann. Acad. | Annales Academiæ Rheno-Trajectinæ |
| Utrecht, Kliniek | Kliniek: Tijdschrift voor Wetenschappelijke Geneeskunde |
| Utrecht, Nieuwe Verh. Prov. Genootsch. | Nieuwe Verhandelingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen |

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| Utrecht, Onderzoek. | Onderzoekingen gedaan in het Physiologisch Laboratorium der Utrechtsche Hoogeschool |
| Utrecht, Scheik. Onderzoek. | Scheikundige Onderzoekingen, gedaan in het Laboratorium der Utrechtsche Hoogeschool |
| Utrecht, Verh. • Prov. Genootsch. | Verhandelingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen |
| Valais Soc. Murith. | See Bull. Murith. |
| Valencia, Act. Med. | Actas del Instituto Medico Valenciano |
| Valenciennes, Mem. Soc. Agric. | Memoires de la Société d'Agriculture, des Sciences, et des Arts, de l'Arrondissement de Valenciennes |
| Valentin, Rep. | Repertorium für Anatomie und Physiologie |
| Van Diemen's Land, Roy. Soc. Papers | Papers and Proceedings of the Royal Society of Van Diemen's Land |
| Van Diemen's Land, Roy. Soc. Reports | Reports of the Royal Society of Van Diemen's Land (For Horticulture, Botany, and the Advance of Science) |
| Van Nostrand's Mag. | Van Nostrand's Engineering Magazine |
| Vargasia | Vargasia: Boletin de la Sociedad de Ciencias fisicas y naturales de Caracas |
| Varsovie Soc. Natur. Trav. | Comptes Rendus et Memoires de la Société des Naturalistes (a l'Universite Imperiale) de Varsovie |
| Varsovie Soc. Natur. Trav. (Mem.) | Travaux de la Société des Naturalistes de l'Universite Imperiale de Varsovie |
| Vaucluse Acad. Mem. | Memoires de l'Academie de Vaucluse |
| Venez. P. | Venezuela Patent |
| Venezia, Ateneo | L'Ateneo Veneto: Rivista mensile di Science, Lettere ed Arti |
| Venezia, Ateneo Eserciz. | Esercitazioni Scientifiche e Letterarie dell' Ateneo di Venezia |
| Venezia, Atti | Atti delle Adunanze dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti |
| Venezia, Atti Ateneo | Atti dell' Ateneo Veneto |
| Venezia, Iat. Atti | Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti |
| Venezia, Ist Mem. | Memorie del Reale Istituto Veneto di Scienze, Lettere ed Arti |
| Venezia, Mem. Ist Beneto | Memorie dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti |
| Ver. Anal. Chem. | See Repert. Anal. Chem. |
| Verh. Genootsch. Occ. Qui Non. | Verhandelingen van het Genootschap: "Occidir qui qui non servat." |
| Verh. Ges. deut. Naturf. Aerzte | Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte |
| Verh. poly. Ges. | Verhandlungen der poltechnischen Gesellschaft |
| Verh. Ver. Gewerbeleis. | Verhandlungen des Vereins zur Beförderung des Gewerbeleisses in Preussen |
| Veröffent. kais. Gesundh. | Veröffentlichungen des kaiserlichen Gesundheitsamts |
| Verona, Soc. Ital. Mem. | Memorie di Matematica e Fisica della Societa Italiana della Scienze |
| Vet. J. London | Veterinary Journal, London |
| Vet. Med. Assoc. Trans. Veterinarian | Transactions of the Veterinary Medical Association The Veterinarian |
| Victoria Dept. Mines Spec. Reports | Victoria. Department of Mines. Special Reports |
| Victoria Field Natur. Club | See Victorian Natlist. |
| Victoria Inst. J. | Journal of the Transactions of the Victoria Institute or Philosophical Society of Great Britain |
| Victoria Natur. | The Victorian Naturalist. The Journal and Magazine of the Field Naturalists' Club of Victoria |

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| Victoria P. | Victoria Patent |
| Victoria Pharm. Soc. J. | Quarterly Journal and Transactions of the Pharmaceutical Society of Victoria |
| Victoria Proc. Roy. Soc. | Proceedings of the Royal Society of Victoria |
| Victoria Trans. Phil. Inst. | Transactions of the Philosophical Institute (afterwards Royal Society) of Victoria |
| Victoria Trans. Roy. Soc. | Transactions of the Royal Society of Victoria |
| Victoria Zool. Soc. Proc. | Proceedings of the Zoological and Acclimatisation Society of Victoria |
| Vierteljahrschr. ärzt. poly. | Vierteljahrsschrift der ärztlichen Polytechnik |
| Vierteljahrschr. gericht. Med. | Vierteljahrsschrift für gerichtliche Medizin und öffentliches Sanitätswesen |
| Vierteljahrschr. gesundheitspf. | Vierteljahrsschrift für Gesundheitspflege |
| Vierteljahrschr. Zahnheilk. | Vierteljahrsschrift für Zahnheilkunde |
| Virchow's Archiv path. | Virchows Archiv für pathologie, Anatomie, und Histologie |
| Viviani, Ann. Bot. | Annali di Botanica |
| Vogel, Notizen | Notizen aus dem Gebeite der practischen Pharmacie |
| Voigt, Mag. | Magazin für den neuesten Zustand der Naturkunden, mit Rücksicht auf die dazu gehörigen Hülfswissenschaften |
| Vosges Soc. Emul. Ann. | Annales de la Société d'Émulation du Département des Vosges |
| W. Austral. P. | West Australian Patent |
| Wag. Free Inst. Sci. Trans. | Transactions of the Wagner Free Institute of Science of Philadelphia |
| Wag. Jahr. | (Wagner's) Jahresbericht über Chemische Technologie |
| Walker, Elect. Mag. | The Electrical Magazine |
| Warwick. Field Club Proc. | Proceedings of the Warwickshire Naturalists' and Archaeologists' Field Club |
| Warwick. Natur. Hist. Soc. Rep. | Annual Reports of the Warwickshire Natural History and Archaeological Society |
| Washburn Obs. Publ. | Publications of the Washburn Observatory of the University of Wisconsin |
| Washington | Int. Med. Congr. Trans., 1887 |
| Washington | See also under U. S. |
| Washington Biol. Soc. Proc. | Proceedings of the Biological Society of Washington |
| Washington, Mem. Natl. Acad. | Memoirs of the National Academy of Sciences |
| Washington, Natl. Inst. Bull. | Bulletin of the Proceedings of the National Institution for the Promotion of Science |
| Washington Phil. Soc. Bull. | Bulletin of the Philosophical Society of Washington |
| Wasser Abwasser | Wasser und Abwasser |
| Water Supply Papers | Water Supply Papers |
| Watford Nat. Hist. Soc. Trans. | Transactions of the Watford Natural History Society and Hertfordshire Field Club |
| Weale, Quart. Papers | Quarterly Papers on Engineering |
| Weber, Archiv | Archiv für die systematische Naturgeschichte |
| Weimer, Zts. Geburtsk. | Gemeinsame Deutsche Zeitschrift für Geburtskunde |
| Weinlaube | Die Weinlaube |
| Wernigerode Naturwiss. Ver. Schr. | Schriften des Naturwissenschaftlichen Vereins des Harzes in Wernigerode |
| West. Brewer | Western Brewer, The |
| West. Chem. Mët. | Western Chemist and Metallurgist |
| West. Drug. | Western Druggist |

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| Westphäl. Prov. Blätt. | Westphälische Provincial-Blätter. Verhandlungen der Gesellschaft zur Beförderung der vaterländischen Cultur in Minden |
| Westphäl. Ver. Jahr. | Jahres-Bericht des Westfälischen Provinzial-Vereins für Wissenschaft und Kunst |
| Wetter | Das Wetter. Meteorologische Montasschrift für Gebildete aller Stände |
| Wetterau. Ges. Ann. | Annalen der Wetterauischen Gesellschaft für die gesammte Naturkunde |
| Wetterau. Ges. Ffstgabe. | Naturhistorische Abhandlungen aus dem Gebiete der Wetterau |
| Wetterau. Ges. Jahr. | Jahresbericht der Wetterauischen Gesellschaft für die gesammte Naturkunde |
| Wetterau. Ges. Naturk. Ber. | Bericht der Wetterauischen Gesellschaft für die gesammte Naturkunde zu Hanau |
| Wiad. Mat. | Wiadomości Matematyczne |
| Wiek's Gewerbeztg. | Deutsche Gewerbezeitung (F. Wiek) |
| Wied. Ann. Phys. | Annalen der Physik und Chemie (Wiedemann's) |
| Wied. Archiv | Archiv für Zoologie und Zootomie |
| Wied. Zool. Mag. | Zoologisches Magazin |
| Wiegmann, Archiv | Archiv für Naturgeschichte |
| Wien Abh. | Naturwissenschaftliche Abhandlungen |
| Wien Akad. Ber. | Sitzungsberichte der kaiserlichen Akademie der Wissenschaften; Mathematisch-Naturwissenschaftliche Klasse, II Abthlg. Wien |
| Wien Akad. Denkschr. | Denkschriften der kaiserlichen Akademie der Wissenschaften. Mathematisch - Naturwissenschaftliche Classe |
| Wien Akad. Sitzber. | Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften |
| Wien Almanach | Almanach der kaiserlichen Akademie der Wissenschaften |
| Wien Alpen-Verein, Jahr. | Jahrbuch des Oesterreichischen Alpen-Vereins |
| Wien Anthropol. Ges. Mitth. | Mittheilungen der Anthropologischen Gesellschaft |
| Wien Anz. | Anzeiger der kaiserlichen Akademie der Wissenschaften: Math.-Naturwissensch. Classe |
| Wien Denkschr. | Denkschriften der kaiserlichen Akademie der Wissenschaften: Mathematisch - naturwissenschaftliche Classe |
| Wien Embryol. Inst. Mitth. | Mittheilungen aus dem Embryologischen Institute der k. k. Universität in Wien |
| Wien Geogr. Ges. Abh. | Abhandlungen der k. k. Geographischen Gesellschaft in Wien |
| Wien Geogr. Ges. Festschr. | Festschrift der k. k. Geographischen Gesellschaft 1884-1898 |
| Wien Geogr. Ges. Mitth. | Mittheilungen der k. k. Geographischen Gesellschaft in Wien |
| Wien Med. Chir. Acad. Abh. | Abhandlungen der k. k. medicinisch-Chirurgischen Josephs-Academie zu Wien |
| Wien Med. Chir. Acad. Beob. | Beobachtungen der k. k. medicinisch-chirurgischen Josephs-Academie zu Wien |
| Wien Naturhist. Hofmus. Ann. | Annalen des k. k. Naturhistorischen Hofmuseums |
| Wien Ornith. Vrr. Mitth. | Mittheilungen des Ornithologischen Vereins in Wien |
| Wien Phot. Corresp. | Photographische Correspondenz. Organ der Photograph. Gesellsch. in Wien |
| Wien Schr. | Schriften des Vereines zur Verbreitung naturwissenschaftlicher Kenntnisse |

- Wien Sitzber. Sitzungsberichte der Mathematisch-naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften
- Wien, Sonnblick-Ver. Jahr. Jahres-Bericht des Sonnblick-Vereines. Wien
- Wieg. technol. Blätter Wiener technologische Blätter
- Wien Ver. Naturwiss. Schriften des Vereins zur Verbreitung Naturwissenschaftlicher Kenntnisse in Wien
- Wien, Ver. Ges. Aerzte. Verhandlungen der k. k. Gesellschaft der Aerzte zu Wien
- Wien Verh. Gewerb-Vereins. Verhandlungen des Niederösterreichischen Gewerb-Vereins
- Wien Wochenbl. Aerzte Wochenblatt der k. k. Gesellschaft der Aerzte in Wien
- Wien Zts. Ges. Aerzte Zeitschrift der k. k. Gesellschaft der Aerzte zu Wien
- Wien, Zool. Bot. Ges. Festschr. Festschrift zur Feier des fünfundzwanzigjährigen Bestehens der k. k. Zoologisch-Botanischen Gesellschaft in Wien
- Wien, Zool. Bot. Verh. Verhandlungen der k. k. Zoologisch-Botanischen Gesellschaft in Wien
- Wien, Zool. Inst. Arb. Arbeiten aus dem Zoologischen Institute der Universität Wien und der Zoologischen Station in Triest
- Wiener Entom. Monatschr. Wiener Entomologische Monatschrift
- Wiener Entom. Ver. Jahr. Jahresbericht des Wiener Entomologischen Vereins
- Wiener Entom. Ztg. Wiener Entomologische Zeitung
- Wiener klin. Wochenschr. Wiener klinische Wochenschrift
- Wiener landw. Ztg. Wiener landwirtschaftliche Zeitung
- Wiener Med. Wochenschr. Wiener medicinische Wochenschrift
- Wiener Mitth. Phot. Wiener Mittheilungen (Photographischen Inhalts)
- Wiener Mus. Ann. Annalen des Wiener Museums der Naturgeschichte
- Wiener Poly. J. Allgemeines Wiener polytechnisches Journal
- Wiener Ztg. Wiener Zeitung
- Wiener Zts. Physik. Zeitschrift für Physik, Chemie, und Mineralogie
- Wild, Rep. Meteorol. Repertorium für Meteorologie, herausg. von der kaiserlichen Akad. der Wissenschaften
- Wilna, Collect. Med. Chir. Collectanea medico-chirurgica Caesarea Academiae Medico-Chirurgicae cura edita
- Wilts, Archaeol. Natur. Magazine of the Archaeological and Natural History Society of Wiltshire
- Hist. Mag. Society of Wiltshire
- Wimereux Lab. (Stat.) See Lille Inst. Zool. Trav.
- Zool.
- Winchester, J. Sci. Soc. Journal of Proceedings and Annual Reports of the Winchester and Hampshire Scientific and Literary Society
- Wisconsin Acad. Trans. Transactions of the Wisconsin Academy of Sciences, Arts, & Letters
- Wisconsin Natur. Hist. Soc. Bull. Bulletin of the Wisconsin Natural History Society
- Wisconsin Natur. Hist. Soc. Pap. Occasional Papers of the Natural History Society of Wisconsin
- Wisconsin Natur. Hist. Soc. Proc. Proceedings of the Natural History Society of Wisconsin
- Wisconsin Univ. Bull. Sci. Bulletin of the University of Wisconsin. Science Series
- Wiss. Abh. Phys.-Tech. Reichsanstalt Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt
- Wiss. Meeresuntersuch. Wissenschaftliche Meeresuntersuchungen herausgegeben von der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel und der biologischen Anstalt auf Helgoland

CXIV LIST OF ABBREVIATIONS TO LITERATURE.

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| Wochenbl. Archit. Ver. | Wochenblatt, herausgegeben von mitgliedern des Architekten-Vereins zu Berlin |
| Wochenbl. Papierfabr. | Wochenblatt der Papierfabriken |
| Wochenschr. Bräu. | Wochenschrift für Brauere |
| Wochenschr. Centr.-Ver. Rubezucker-ind. | Wochenschrift des Central-Vereins für Rubenzucker-industrie in der Oesterr.-Ung.-Monarchie |
| Wochenschr. österr. Ing. Ver. | Wochenschrift des österreichischen Ingenieur und Architekten Vereins |
| Wochenschr. Ver. deut. Ing. | Wochenschrift des Vereins deutscher Ingenieure |
| Wollen-Gewerbe | Das Deutsche Wollen-Gewerbe |
| Wollen Ztg. | Wollen Zeitung |
| Wombat | The Wombat. The Journal of the Geelong Field Naturalists' Club, and the Gordon College Amateur Photographic Association |
| Woods Holl Mar. Biol. Lab. Bull. | Biological Bulletin. Edited by the Director and Members of the Staff, of the Marine Biological Laboratory, Woods Holl, Mass. |
| Woods Holl Mar. Biol. Lab. Lect. | Biological Lextures delivered at (from) the Marine Biological Laboratory (of) Woods Holl (Mass.) |
| Woolhope Field Club Trans. | Transactions of the Woolhope Naturalists' Field Club |
| Woolwich, Proc. | Minutes of Proceedings of the Royal Artillery Institution |
| World's Paper Trade Rev. | World's Paper Trade Review |
| Wunderlich, Archiv. Heilk. | Sée Roser und Wunderlich |
| Württemberg. Aerzt. Ver. Mitth. | Mittheilungen des Württembergischen Aerztlichen Vereins |
| Württemberg, Jahresh. | Jahreshefte des Vereins für vaterländische Naturkunde in Württemberg |
| Würzburg, Arb. Bot. Inst. | Arbeiten des Botanischen Instituts in Würzburg |
| Würzburg, Arb. Phys. Lab. | Arbeiten aus dem Physiologischen Laboratorium der Würzburger Hochschule |
| Würzburg. Med. Zts. | Würzburger medicinische Zeitschrift |
| Würzburg. Naturwiss. Zts. | Würzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft |
| Würzburg Phys. Med. Festschr. | Festschrift zur Feier ihres fünfzigjährigen Bestehens herausgegeben von der Physikalisch-Medizinischen Gesellschaft zu Würzburg |
| Würzburg, Phys. Med. Sitzber. | Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg |
| Würzburg, Phys. Med. Verh. | Verhandlungen der Physikalisch-Medicinischen Gesellschaft |
| Würzburg, Zool Inst. Arb. | Arbeiten aus dem Zoologisch-Zootomischen Institut in Würzburg |
| Year Book Pharm. | See Brit. Pharm. Confer. Proc. |
| Year-book of Pharm. | Year-book of Pharmacy |
| Yn Lioar Manninagh | Yn Lioar Manninagh. The Journal of the Isle of Man Natural History and Antiquarian Society |
| Yokohama, Mitth. Deut. Ges. | Mittheilungen der Deutschen Gesellschaft für Natur und Völkerkunde Ostasiens |
| Yonne | See Auxere |
| Yonne, Bull. | Bulletin de la Société des Sciences Historiques et Naturelles de l'Yonne |
| Yorksh. Natur. Union Trans. | The Transactions of the Yorkshire Naturalists' Union |
| Yorksh. Phil. Soc. Report | Annual Report of the Council of the Yorkshire Philosophical Society |

LIST OF ABBREVIATIONS TO LITERATURE

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| Yorksh. Proc. Phil. Soc. | Proceedings of the Yorkshire Philosophical Society |
| Zach, Corresp. | Correspondence Astronomique, Geographique, Hydrographique, et Statistique |
| Zach, Monat. Corresp. | Monatliche Correspondenz zur Beförderung der Erd- und Himmels-Kunde |
| Zahntech. | Die Zahntechnische Reform |
| Zantedeschi, Ann. Fis. | Annali di Fisica |
| Zeeuwsch Genootsch. | Nieuwe Verhandelingen van het Zeeuwsch Genootschap der Wetenschappen |
| Nieuwe Verh. | |
| Zeeuwsch Genootsch. Wet. Archief | Archief Vroegere en Latere Mededeelingen voornamelijk in Betrekking tot Zeeland, uitgegeven door het Zeeuwsch Genootschap der Wetenschappen |
| Zentr. Biochem. Biophys. | Zentralblatt für Biochemie und Biophysik |
| Zentr. exp. Med. | Zentralblatt der experimentellen Medizin (former name Zentralblatt für die gesamte Physiologie und Pathologie des Stoffwechsels) |
| Zentr. inn. Med. | Zentralblatt für innere Medizin |
| Zentr. oesterr - ungar Papierind. | Zentralblatt für die oesterr-ungar Papierindustrie |
| Zentr. Physiol. | Zentralblatt für Physiologie |
| Zentr. Physiol. Path. Stoffwech. | Zentralblatt für die gesamte Physiologie und Pathologie des Stoffwechsels, Berlin und Wien |
| Zeuner, Civilingenieur | Der Civilingenieur, Zeitschrift für das Ingenieurwesen |
| Ziva | Ziva: Casopis prirodnicky |
| Zool. Anz. | Zoologischer Anzeiger |
| Zool. Beitr. | Zoologische Beiträge |
| Zool. Bull. | Zoological Bulletin |
| Zool. Congr. | See Congr. Int. Zool. C. R. Int. Congr. Zool. Proc. |
| Zool. Jahr. | Zoologische Jahrbücher. Zeitschrift für Systematik, Geographie und Biologie der Thiere |
| Zool. J. | The Zoological Journal |
| Zool. Soc. Proc. | Proceedings of the Scientific Meetings (General Meetings for Scientific Business) of the Zoological Society of London |
| Zool. Soc. Trans. | Transactions of the Zoological Society of London |
| Zool. Vortr. | Zoologische Vorträge |
| Zoologica | Zoologica. Original-Abhandlungen aus dem Gesamtgebiete der Zoologie |
| Zoologist | The Zoologist; a monthly Journal of Natural History |
| Ztg. Blechind. | Illustrierte Zeitung für Blechindustrie |
| Zts. Akklimat. | Zeitschrift für Akklimatisation: Organ des Akklimatisations-Vereins in Berlin |
| Zts. allg. Erdkunde | Zeitschrift für allgemeine Erdkunde |
| Zts. allg. österr. Apoth.-Ver. | Zeitschrift des allgemeinen österreichischen Apothekervereins |
| Zts. allg. Physiol. | Zeitschrift für allgemeine Physiologie |
| Zts. anal. Chem. | Zeitschrift für analytische Chemie |
| Zts. Anat. | Zeitschrift für Anatomie und Entwicklungsgeschichte |
| Zts. ang. Chem. | Zeitschrift für angewandte Chemie, und Zentralblatt für technische Chemie |
| Zts. ang. Mikr. | Zeitschrift für angewandte Mikroskopie mit besonderer Rücksicht auf die mikroskopischen Untersuchungen von Nahrungs- und Genussmitteln, technischen Produkten, Krankheitsstoffen, etc. |
| Zts. anorg. Chem. | Zeitschrift für anorganische Chemie |
| Zts. Bauwesen | Zeitschrift für Bauwesen |
| Zts. Berg-Hütten Salinenw. | Zeitschrift für das Berg-Hütten und Salinenwesen im Preussischen Staate |
| Zts. Biol. | Zeitschrift für Biologie |

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| Zts. Bot. | Zeitschrift für Botanik |
| Zts. Chem. | Zeitschrift für Chemie |
| Zts. chem. Apparat. | Zeitschrift für chemische Apparatentechnik (Discontinued) |
| Zts. Chem. Ind. | Zeitschrift für die Chemische Industrie mit besonderer Berücksichtigung der chemisch-technischen Untersuchungsverfahren 1887; later Zts. ang. Chem. |
| Zts. chem. Ind. Kolloide | Zeitschrift für Chemie und Industrie der Kolloide |
| Zts. Chemotherap. | Zeitschrift für Chemotherapie und verwandte Gebiete. (formerly Folia Serologia) |
| Zts. deut. geol. Ges. Abh. | Zeitschrift der deutschen geologischen Gesellschaft Abhandlungen |
| Zts. deut. Landw. | Zeitschrift für deutsche Landwirthe |
| Zts. Dreschler | Zeitschrift für Dreschler, Elfenbeingraveur und Holzbildhauer |
| Zts. Düngerw. | Zeitschrift für Düngerwesen |
| Zts. Electrochem. | Zeitschrift für Electrochemie |
| Zts. Entom. (Breslau) | Zeitschrift für Entomologie im Auftrage des Vereins für schlesische Insektenkunde zu Breslau |
| Zts. Ethnol. | Zeitschrift für Ethnologie |
| Zts. exper. Path. Therap. | Zeitschrift für experimentelle Pathologie und Therapie, Berlin |
| Zts. Farben-Ind. | Zeitschrift für Farben-Industrie |
| Zts. Feuerwehr. | Illustrierte Zeitschrift für die deutsche Feuerwehr |
| Zts. Fischerei | Zeitschrift für Fischerei |
| Zts. Fleisch. Milchhyg. | Zeitschrift für Fleisch- und Milchhygiene |
| Zts. Geburtsh. | Zeitschrift für Geburtshilfe und Frauenkrankheiten |
| Zts. Geburtsh. Gynäkol. | Zeitschrift für Geburtshilfe und Gynäkologie |
| Zts. ges. Brauw. | Illustrierte Zeitschrift das gesamte Brauwesen |
| Zts. ges. Getreidew. | Zeitschrift für das gesamte Getreidewesen |
| Zts. ges. Naturwiss. | Zeitschrift für die Gesamten Naturwissenschaften |
| Zts. Ges. Ornith. | Zeitschrift für die gesamte Ornithologie |
| Zts. ges. Textilind. | Zeitschrift für die gesamte Textilindustrie |
| Zts. ges. Wasserwirts. | Zeitschrift für die gesamte Wasserwirtschaft |
| Zts. Heilk. | Zeitschrift für Heilkunde, als Fortsetzung der Prager Vierteljahrschrift für praktische Heilkunde |
| Zts. Hyg. | Zeitschrift für Hygiene und Infektionskrankheiten |
| Zts. Immunit. Abt. I. 13. | Zeitschrift für Immunitätsforschung und experimentelle Therapie. Abteilung I. 13. Abteilung II. or Ref. 1 vol. |
| Abt. Ref. | |
| Zts. Induk. Abst. Vererbungslehre | Zeitschrift für Induktive Abstammungs- und Vererbungslehre |
| Zts. Instrumentenk. | Zeitschrift für Instrumententechnik |
| Zts. Klin. Med. | Zeitschrift für Klinische Medizin |
| Zts. Krebsforsch. | Zeitschrift für Krebsforschung |
| Zts. Kryst. Mineral. | Zeitschrift für Krystallographie und Mineralogie |
| Zts. landw. Versuchsw. | Zeitschrift für das landwirtschaftliche Versuchswesen in Oesterreich |
| Zts. Malakozool. | Zeitschrift für Malakozoologie |
| Zts. Math. Phys. | Zeitschrift für Mathematik und Physik |
| Zts. math. Unterr. | Zeitschrift für mathematischen und naturwissenschaftlichen Unterricht |
| Zts. Mikro. Tek. | Zeitschrift für Mikroskopische Technik. |
| Zts. Morphol. Anthropol. | Zeitschrift für Morphologie und Anthropologie |
| Zts. Nahr. Genuss. (Z. genuss) | Zeitschrift für Untersuchung der Nahrungs- und Genussmittel, sowie der Gebrauchsgegenstände |
| Zts. Naturwiss. | Zeitschrift für Naturwissenschaften im Auftrage (Organ) des Naturwissenschaftlichen Vereins für Sachsen und Thüringen |

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| Zts. öffentl. Chem. | Zeitschrift für öffentliche Chemie |
| Zts. Ohrenheilk. | Zeitschrift für Ohrenheilkunde in deutscher und englischer Sprache |
| Zts. österr. Ing. Ver. | Zeitschrift des österreichischen Ingenieur und Architekten Vereins |
| Zts. paraf. Ind. | Zeitschrift für Parafin Industrie |
| Zts. Parasit. | Zeitschrift für Parasitenkunde |
| Zts. Pflanzenkrankheiten | Zeitschrift für Pflanzenkrankheiten |
| Zts. physik. Chem. | Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre |
| Zts. Physik. Chem. Unterr. | Zeitschrift für den physikalischen und chemischen Unterricht |
| Zts. Physiol. Chem. | Zeitschrift für physiologische Chemie (Hoppe-Seylers) |
| Zts. prakt. Geol. | Zeitschrift für praktische Geologie |
| Zts. Psychol. | Zeitschrift für Psychologie und Physiologie der Sinnesorgane |
| Zts. ration. Med. | Zeitschrift für rationelle Medicin |
| Zts. Reprodukt. | Zeitschrift für Reproduktionstechnik |
| Zts. Rübenzuckerind. | Neue Zeitschrift für Rübenzuckerindustrie |
| Zts. Schiess Spreng. | Zeitschrift für das gesammte Schiess- und Sprengstoffwesen |
| Zts. Spiritusind. | Zeitschrift für Spiritusindustrie |
| Zts. Telegr. Ver. | Zeitschrift des deutsch-österreichischen Telegraphen-Vereins |
| Zts. Thiermed. | Zeitschrift für Thiermedizin |
| Zts. Tuberkulose | Zeitschrift für Tuberkulose und Heilstättenwesen |
| Zts. Ver. deut. Ingen. | Zeitschrift des Vereins deutscher Ingenieure |
| Zts. Ver. Rübenzuckerind. | Zeitschrift des Vereins für die Rübenzucker-Industrie des deutschen Reichs |
| Zts. Ver. Zuckerind. | Zeitschrift des Vereins der deutschen Zuckerindustrie |
| Zts. Wiss. Geogr. | Zeitschrift für wissenschaftliche Geographie |
| Zts. wiss. Mikro. | Zeitschrift für wissenschaftliche Mikroskopie |
| Zts. wiss. Photochem. | Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie |
| Zts. wiss. Zool. | Zeitschrift für wissenschaftliche Zoologie |
| Zts. Zuckerind. | Zeitschrift für Zuckerindustrie |
| Zts. Zuckerind. Böhm. | Zeitschrift für Zuckerindustrie in Böhmen |
| Zürich Denkschr. Med. | Denkschrift der medizinisch-chirurgischen Gesellschaft des Kantons Zürich |
| Chir. Ges. | |
| Zürich Mitth. | Mittheilungen der Naturforschenden Gesellschaft in Zürich |
| Zürich, Monats. | Monatsschrift des wissenschaftlichen Vereins in Zürich |
| Zürich naturf. Ges. | Vierteljahrsschrift der naturforschenden Gesellschaft in Zürich |
| Zürich Physik. Ges. Jahr. | ... Jahresbericht der physikalischen Gesellschaft in Zürich |
| Zürich, Schweiz. Ges. Neue Denkschr. | Neue Denkschriften der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften |
| Zürich, Soc. Entom. | Societas Entomologica. Organ für den internationalen Entomologenverein. Zürich |
| Zürich, Unters. Physiol. Lab. | Untersuchungen aus dem Physiologischen Laboratorium der Züricher Hochschule |
| Zürich, Verh. | Verhandlungen der Medicinisch-chirurgischen Gesellschaft des Kanton Zürich im Jahr 1826 |
| Zürich, Vierteljahrsschr. | Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich |
| Zwickau Ver. Naturk. Jahr | Jahresbericht des Vereins für Naturkunde zu Zwickau |
| Zwolle, Vooruitgang. | De Vooruitgang; Tijdschrift voor Wetenschap |

CHAPTER V.

NITRIC ACID.

Historical. The first theory as to the composition of nitric acid was enunciated by Mayow in 1669,¹ who believed that the acid contained two components, one derived from the air and of a fiery nature, and the other obtained from the earth. It was not until more than a century later, in 1776, that Lavoisier² showed that one constituent of nitric acid was oxygen; and it remained for Cavendish to prove the exact composition and mode of formation of this acid by the direct union of gaseous nitrogen and oxygen in the presence of water or alkaline solutions.³ Bunsen⁴ showed that nitric acid is produced when various substances are burned in an atmosphere of oxygen and nitrogen. Similarly,⁵ if hydrogen be burned in a flask containing oxygen, nitric acid is formed in notable quantity.

For many years⁶ nitric acid of higher concentration than

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2. Phil. Trans. 1784, **74**, 119; 1785, **75**, 372.
3. Cavendish, Phil. Trans. 1785, **75**, 379.
4. Gasometry, 58.
5. Kolbe, Ann. 1861, **119**, 176; Hofmann, Ber. 1870, **3**, 663.
6. Anon., Electrician, 1902, **49**, 684. Anon., Engineering (London), 1905, **81**, 89; Engineer, 1906, **102**, 286; Eclairage Electrique, 1906, **16**, 297. Anon., Zts. Electrochem. 1907, **13**, 75. Anon., Board of Trade J. Aug. 19, 1909; J. S. C. I. 1909, **28**, 937. Anon., Census Bur. Rept., through Oil, Paint and Drug Rept., Nov. 27, 1911; abst. C. A. 1912, **6**, 2499. Anon., Engineering (London), 1914, **98**, 267. Anon., Eng. News, 1915, **73**, 16. Anon., Chem. Ztg. April 23, 1914. Anon., Zts. Vereins Deut. Ing. 1914, **58**, 66. Anon., Chem. Trade J. 1915, **56**, 311; abst. C. A. 1915, **9**, 2130. Anon., Elektrochem. Zts. 1915, **21**, 211. Anon., Engineering (London), 1916, **102**, 440. Anon., Colliery Guardian, 1917, **114**, 68; abst. C. A. 1917, **11**, 3419. Abegg Handb. anorg. Chem. 1907, **3**, 3, 145. W. Adam, Chem. Trade J. 1918, **62**, 181; abst. J. S. C. I. 1918, **37**, A, 179. R. Adams and C. Beebe, J. A. C. S. 1916, **38**, 2768; abst. J. S. C. I. 1917, **36**, 100. B. Adhikary, Chem. News, 1915, **112**, 163; abst. J. S. C. I. 1915, **34**, 1053; see also J. S. C. I. 1911, **30**, 282. A. Aengstroem, Ann. Pogg. 1871, **144**, 300 (Jubelb. 1874, 424); Compt. rend. 1871, **73**, 369; Phil. Mag. 1871, **42**, 395; Ann. de Chim. 1872, **26**, 255. Aktiebolaget Nitrogenium, Swed. P. 43816, 1918; abst. C. A. 1918, **12**, 2689. Alexander, James and Vint, E. P. Appl. 11256, 1917; abst. J. S. C. I. 1917, **36**, 78. A. Allen, Chem. News, 1879, **40**, 135; 1880, **41**, 231; Eng. Min. J. 1917, **103**, 230; abst. C. A. 1917, **11**, 1020. W. Allen, Eighth Inter. Cong. Appl. Chem. 1912, **1**, 19; abst. J. S. C. I. 1912, **31**, 921. H. Alt, Ann. (Drude), 1904, **13**, 1010. E. Amagat, Compt. rend. 1879, **88**,

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sulfuric acid, and distillation of the nitric acid formed,

(2) Manufacture from the atmosphere by oxidation.

(3) The catalytic oxidation of ammonia to nitric acid.

* Each of these processes, with their modifications,* is described herewith in detail.

Nitrogen. Rutherford in 1772¹ showed that when animals breathe in a closed volume of air, it contains a constituent which is incapable of supporting combustion or respiration. The same

1910, **11**, 1228; abst. Met. Chem. Eng. 1911, **9**, 73. T. Zoeller and E. Grete, Ber. 1877, **10**, 2145. See also Nitric acid, Chem. News, 1861, **4**, 157; 1862, **5**, 69; 1870, **21**, 190; 1871, **24**, 134, 146, 158, 311; 1874, **30**, 83; 1876, **33**, 255; 1878, **38**, 19; 1883, **47**, 282; 1885, **52**, 297; 1891, **64**, 85; 1892, **65**, 37; 1908, **98**, 90.

Chloroform as an antidote for Nitrous Fumes. J. S. C. I. 1904, **23**, 265, 772; Met. Chem. Eng. 1912, **10**, 126. Newspaper clippings, Times, Raleigh, N. C., June 14, 1912, Wall Street Journal, July 25, 1912. Forty-ninth annual report on Alkali, Proceedings during the year 1912; abst. J. S. C. I. 1913, **32**, 768. Met. Chem. Eng. 1913, **11**, 42; Eng. Mining J. 1913, **95**, 602. Times Engineering Supplement, Oct. 15, 1913; abst. J. S. C. I. 1913, **32**, 1008. Chem. Zts. 1914, **13**, 117; abst. J. Ind. Eng. Chem. 1914, **6**, 778. Chem. Ztg. 1914, **38**, 593; abst. J. Ind. Eng. Chem. 1914, **6**, 597. J. S. C. I. 1914, **33**, 134. Met. Chem. Eng. 1914, **12**, 265. Zts. Vereines deutschen Ingenieure, 1914, **58**, 66, 980. Elektrochem. Zts. 1915, **21**, 211. Met. Chem. Eng. 1915, **13**, 456, 638. Electrical World, 1916, **68**, 67, 69. Frankfurter Handelsblatt, May 29, 1916; abst. Engineering, 1916, **101**, 576. Nature, 1916, **97**, 19. Sci. Amer. 1916, **112**, 216. Nitrate Supply Committee recommendations on synthetic nitric acid for the government, with reports on various methods, J. Ind. Eng. Chem. 1917, **9**, 829; abst. C. A. 1917, **11**, 3384. 53rd Report on Alkali Works, 1916, 21; abst. J. S. C. I. 1917, **36**, 997. See also J. S. C. I. 1915, **34**, 1001.

Bd. of Trade J. July 3, 1902; abst. J. S. C. I. 1902, **21**, 1002; Chem. Ind. 1903, **26**, 576; abst. J. S. C. I. 1903, **21**, 1315. Chem. Trade J. Dec. 28, 1901; abst. J. S. C. I. 1902, **21**, 80. Chem. Trade J. 1916, **58**, 28; abst. J. S. C. I. 1916, **35**, 953. Chem. Trade J. 1918, **63**, 25; abst. C. A. 1918, **12**, 2035. Dipl. and Cons. Reps. Dec. 1902; abst. J. S. C. I. 1903, **22**, 52. Electrician, 1902, 684; abst. J. S. C. I. 1902, **21**, 1138, 1143. Elec. World, 1918, **72**, 894; abst. C. A. 1919, **13**, 8. Electrochem. Met. Ind. **6**, 515; abst. C. A. 1909, **3**, 1671. Engineering, Nov. 3, 1916; abst. J. S. C. I. 1916, **35**, 1154. Engineering, 1918, **106**, 154; abst. C. A. 1918, **12**, 2309. Eng. Mining J. July 26, 1902; abst. J. S. C. I. 1902, **21**, 1112. Eng. and Mining J. Jan. 1, 1909; abst. J. S. C. I. 1909, **28**, 139. Foreign Office Ann. Series No. 2885; abst. J. S. C. I. 1902, **21**, 1205. Jahr. der Elektrochemie, 1901, **8**, abst. J. S. C. I. 1902, **21**, 1477. J. Gas Lighting, 1916, **134**, 74; abst. J. S. C. I. 1916, **35**, 466. J. S. C. I. 1902, **21**, 167; 1918, **37**, R, 77, 210. Met. and Chem. 1918, **18**, 534. Oil, Paint and Drug Rep. June 24, July 25, 1912; June 22, 1914; abst. J. S. C. I. 1912, **31**, 686, 772; 1914, **33**, 749. Pharm. J. Nov. 29, 1902; Sept. 11, 1915; Oct. 2, 1915; abst. J. S. C. I. 1902, **21**, 1479; 1915, **34**, 958, 1050. Times Eng. Suppl. Oct. 15, 1913; abst. J. S. C. I. 1913, **32**, 1008. U. S. Cons. Reps. April 15; abst. J. S. C. I. 1903, **22**, 582. U. S. Cons. Reps. No. 1789; Oct. 31, 1903; abst. J. S. C. I. 1903, **21**, 1266. U. S. Comm. Rept. No. 303, Dec. 28, 1915; abst. J. S. C. I. 1916, **35**, 304. J. S. C. I. 1919, **38**, 87-R.

1. Rutherford, De aere Mephitico, Edinburgh, 1772. In this connection see H. Cavendish, Phil. Trans. 1786, **75**, 372.

year J. Priestley found that when carbon is burned in a confined space, one-fifth of the "common" air is converted into "fixed" air, a residual (phlogisticated) air being left. The gas left after the removal of oxygen from purified air, was supposed until 1894 to be pure nitrogen when Ramsay and Ralsigh¹ showed the presence of 1.186% of mixed gases composed of the elements of the helium group.

All nitrogen in the plant and animal kingdom originally came from the nitrogen of the air, the vegetarian animals excreting this element chiefly as hippuric acid, while the carnivora eliminate it primarily as urea and affiliated bodies. These in turn—aided by fermentative and bacterial processes—transform the N back to the elemental form, where the metabolism is repeated. It has been computed² that yearly four hundred million tons of atmospheric nitrogen are thus absorbed and in turn set free. Under the influence of electricity nitrogen becomes more reactive, and unites with atmospheric oxygen to form NO, which in turn oxidizes to NO₂, and this when dissolved by falling rain forms nitrous and nitric acids, which in turn combine with bases in the soil, combining the nitrogen in an available fertilizing form. Certain of the Leguminosae, by means of bacterial colonies which form a nidus in rootlet tubercles, absorb large amounts of nitrogen during their growth, a fact that has been realized for some time, and has been taken advantage of in the rotation of crops. Plants absorb their nitrogen in the form of ammonia, nitrites and nitrates, the former being changed into the two latter by nitrification, i. e., the bacterial oxidation of ammonia into nitrites and nitrates, in two separate stages by entirely different classes of microorganisms. Reversible to nitrification is denitrification, in which directly or indirectly the nitrate is degraded to elemental nitrogen again. This cycle proceeds in nature indefinitely.

Nitrates were, until quite recently, obtained almost exclusively from the supply of sodium nitrate in Chili and other localities, but the demands of the recent war have caused the perfection of synthetic electrolytic processes, whereby it appears that the Chili sodium nitrate industry is faced with serious competition.

1. Phil. Trans. 1895, **186**, 187; J. C. S. 1897, **71**, 181.
2. S. Arrhenius, "Das Werden der Welten," 1908, 130-131.

if, indeed, it is in all probability not doomed to extinction.*

The nitrogen problem is unique in respect to the fact that the material is ever present in unlimited quantities, the proposi-

1. For additional data on the development of nitrogen, consult U. S. P. 207086, 225730, 226632, 227027, 269309, 291163, 569591, 594435, 598918, 605694, 754474, 802980 (abst. J. S. C. I. 1905, **24**, 1254), 923846, 928476, 982288, 984605, 993017, 999003, 1015566 (abst. J. S. C. I. 1912, **33**, 187), 1036788, 1050902, 1056244, 1078423, 1084774, 1096392, 1096393, 1098139, 1914; abst. J. S. C. I. 1914, **33**, 788. 1123394, 1134583 (abst. J. S. C. I. 1915, **34**, 552), 1138190, 1915; abst. J. S. C. I. 1915, **34**, 661. 1150337, 1154145, 1154171, 1154172 (abst. J. S. C. I. 1915, **34**, 1144), 1166294, 1239516. E. P. 2514, 1855; 2607, 1859; 1027, 1416, 1617, 1860; 932, 1861; 1833, 1865; 2801, 1867; 255, 2137, 3752, 1869; 37, 1872; 4013, 1873; 4359, 1877; 4544, 1878; 1446, 1592, 2559, 1879; 1004, 1416, 5478, 1880; 1897, 3728, 5617, 1881; 2263, 3089, 1883; 17106, 1884; 157, 7657, 1885; 3469, 15165, 1886; 36987, 1887; 1844, 3880, 3967, 15173, 1888. E. P. 7851, 1890; Chem. Centr. 1891, **62**, II, 367. E. P. 10331, 14925, 16049, 1890; Chem. Centr. 1892, **63**, I, 358. E. P. 9457, 15975, 1891; Chem. Centr. 1892, **63**, II, 768. E. P. 4411, 11504, 15513, 19078, 1892; Chem. Centr. 1893, **64**, II, 958. E. P. 10442, 1895; Chem. Ztg. 1896, **20**, 877. E. P. 21299, 1898; 17692, 1899. E. P. 9142, 1900; J. S. C. I. 1902, **21**, 345. E. P. 19074, 1900; J. S. C. I. 1901, **20**, 1209; Mon. Sci. 1902, **58**, 154; Chem. Ztg. 1902, **26**, 206. E. P. 19254, 1900; J. S. C. I. 1901, **20**, 1194. E. P. 1339, 11609, 1902; J. S. C. I. 1903, **22**, 795. E. P. 12194, 1902; J. S. C. I. 1902, **21**, 1126. E. P. 16615, 1902; J. S. C. I. 1903, **22**, 995. E. P. 17609, 1902; J. S. C. I. 1903, **22**, 907. E. P. 20053, 1902; J. S. C. I. 1903, **22**, 1130. E. P. 25242, 1902; J. S. C. I. 1903, **22**, 1085. E. P. 1456, 5649, 1903; J. S. C. I. 1904, **23**, 442. E. P. 11126, 1903; J. S. C. I. 1903, **22**, 1045. E. P. 11221, 1903; J. S. C. I. 1903, **22**, 907. E. P. 14213, 1903; J. S. C. I. 1904, **23**, 787. E. P. 14303, 1903; J. S. C. I. 1903, **22**, 1347. E. P. 16298, 1903; J. S. C. I. 1904, **23**, 606. E. P. 28682, 1903; J. S. C. I. 1904, **23**, 750. E. P. 12358, 1904; J. S. C. I. 1904, **23**, 1147. E. P. 13638, 1904; J. S. C. I. 1905, **24**, 793. E. P. 14431, 1904; J. S. C. I. 1904, **23**, 1215. E. P. 29475, 1904; 17946, 1905; J. S. C. I. 1905, **24**, 1161. E. P. 22225, 1905; abst. J. S. C. I. 1906, **25**, 495. E. P. 3994, 4409, 1906; J. S. C. I. 1907, **26**, 318. E. P. 10581, 1906; J. S. C. I. 1907, **26**, 469. E. P. 25605, 1906; J. S. C. I. 1907, **26**, 1090. E. P. 16963, 1908; J. S. C. I. 1909, **28**, 939. E. P. 19402, 1908; J. S. C. I. 1909, **28**, 1088. E. P. 25535, 1908; J. S. C. I. 1909, **28**, 794. E. P. 7307, 1909; J. S. C. I. 1909, **28**, 1249. E. P. 17960, 20631, 1909; J. S. C. I. 1910, **29**, 277; Chem. Ztg. Rep. 1910, **34**, 323. E. P. 25808, 1909; abst. J. S. C. I. 1910, **29**, 1448. E. P. 4362, 1910; abst. J. S. C. I. 1911, **30**, 406. E. P. 8211, 1910; J. S. C. I. 1910, **29**, 1092. E. P. 12748, 1910; J. S. C. I. 1911, **30**, 72. E. P. 24413, 1910; J. S. C. I. 1911, **30**, 621. E. P. 12307, 1911; C. A. 1912, **6**, 3169; J. S. C. I. 1911, **30**, 1314. E. P. 12308, 1911; C. A. 1912, **6**, 3169; J. S. C. I. 1911, **30**, 1383. E. P. 14631, 1911; C. A. 1913, **7**, 222; J. S. C. I. 1912, **31**, 1031; Mon. Sci. 1916, **83**, 41; Chem. Ztg. Rep. 1913, **37**, 33. E. P. 17666, 1911; C. A. 1913, **7**, 403; J. S. C. I. 1912, **31**, 129. E. P. 22531, 1911; abst. C. A. 1913, **7**, 1268; J. S. C. I. 1912, **31**, 535. E. P. 25532, 1911; abst. C. A. 1913, **7**, 1608; J. S. C. I. 1913, **32**, 18. E. P. 25532, 1911; abst. C. A. 1913, **7**, 1608; J. S. C. I. 1913, **32**, 18. E. P. 28075, 1911; abst. J. S. C. I. 1912, **31**, 658. E. P. 3147, 1912; abst. C. A. 1913, **7**, 2457; J. S. C. I. 1913, **32**, 364; Chem. Ztg. Rep. 1913, **37**, 476. E. P. 10718, 1912; abst. C. A. 1913, **7**, 3534; J. S. C. I. 1912, **31**, 1032. E. P. 12051, 1912; abst. C. A. 1913, **7**, 3645; J. S. C. I. 1913, **32**, 289. E. P. 12845, 1912; abst. C. A. 1913, **7**, 2839; J. S. C. I. 1913, **32**, 363; Chem. Ztg. Rep. 1913, **37**, 247. E. P. 14607, 1912; abst. C. A. 1913, **7**, 4050; J. S. C. I. 1913, **32**, 486; Chem. Ztg. Rep. 1913, **37**, 634. E. P. 17431, 1912; abst. J. S. C. I. 1913, **32**, 808. E. P. 16855, 1912; abst. C. A. 1914, **8**, 423; J. S. C. I. 1913,

tion being to render it available economically. The atmosphere enveloping the globe near its surface consists of about 78% nitrogen by volume, the balance being oxygen. The solid crust

32, 902. E. P. 25629, 1912; abst. C. A. 1914, **8**, 1498; J. S. C. I. 1913, **32**, 751; Chem. Ztg. Rep. 1914, **38**, 171. E. P. 3662, 1910; abst. C. A. 1914, **8**, 2607; J. S. C. I. 1913, **32**, 1011. E. P. 12927, 1913; abst. C. A. 1914, **8**, 3842; J. S. C. I. 1914, **33**, 788. E. P. 21211, 1913; abst. J. S. C. I. 1914, **33**, 831. E. P. 28737, 1913; abst. J. S. C. I. 1914, **33**, 483; Mon. Sci. 1917, **84**, 37. E. P. 30073, 1913; abst. J. S. C. I. 1916, **35**, 738. E. P. 6739, 1914; abst. J. S. C. I. 1915, **34**, 552. E. P. 9974, 1914; abst. J. S. C. I. 1915, **34**, 872. E. P. 5097, 1915; abst. J. S. C. I. 1916, **35**, 538. E. P. 100930, F. P. 9727, 1850; 13001, 1852; 22623, 1855; 31926, 1857; 32368, 1857; 40568, 1859; 42891, 1859; 50395, 1861; 52253, 1861; 54954, 1862; 56342, 1862; 57430, 1863. F. P. 14941; abst. Mon. Sci. 1883, **25**, 613. F. P. 322600, 321860, 1902; abst. J. S. C. I. 1903, **22**, 298. F. P. 328245; abst. Mon. Sci. 1904, **61**, 48. F. P. 328600, 1902; J. S. C. I. 1903, **22**, 664. F. P. 328770, 328984, 330258, 1903; abst. J. S. C. I. 1903, **22**, 995, 996, 1087. F. P. 332662, 1903; abst. J. S. C. I. 1903, **22**, 1243. F. P. 332811; abst. Mon. Sci. 1904, **61**, 71. F. P. 338964, 339730; abst. Mon. Sci. 1906, **65**, 3; 1911, **75**, 571, 572. F. P. 348189; abst. Mon. Sci. 1906, **65**, 16; Chem. Ztg. 1905, **29**, 493. F. P. 352254; abst. Mon. Sci. 1906, **65**, 103. F. P. 353467; abst. Mon. Sci. 1906, **65**, 106; Chem. Ztg. 1905, **29**, 1056. F. P. 354073; abst. Mon. Sci. 1906, **65**, 108. F. P. 358171; abst. Mon. Sci. 1906, **65**, 128. F. P. 358373; abst. Mon. Sci. 1906, **65**, 128; Chem. Ztg. 1906, **30**, 224. F. P. 370977, 371397; abst. Chem. Ztg. Rep. 1907, **31**, 140. F. P. 372099; abst. Chem. Ztg. Rep. 1907, **31**, 168. F. P. 379437; abst. Mon. Sci. 1911, **75**, 571, 572, 573. F. P. 380121; abst. Mon. Sci. 1909, **71**, 100; Chem. Ztg. Rep. 1907, **31**, 635. F. P. 385193; abst. Mon. Sci. 1911, **75**, 571, 573; Chem. Ztg. Rep. 1908, **32**, 333. F. P. 387874, 394557; abst. Chem. Ztg. Rep. 1909, **33**, 132. F. P. 400308, 405493, 409787, 1909; abst. J. S. C. I. 1910, **29**, 817. F. P. 410933, 410967, 416224; abst. C. A. 1912, **6**, 1966; Chem. Ztg. Rep. 1910, **34**, 569. F. P. 423328; abst. C. A. 1912, **6**, 2001; Mon. Sci. 1913, **79**, 117; Chem. Ztg. Rep. 1911, **35**, 308. F. P. 423462; abst. C. A. 1912, **6**, 1969; Mon. Sci. 1913, **79**, 117; Chem. Ztg. Rep. 1911, **35**, 306. F. P. 430092, 1911; abst. J. S. C. I. 1911, **30**, 1253. F. P. 432789, 432810, 433239, 1911; abst. J. S. C. I. 1912, **31**, 187. F. P. 433397; abst. Mon. Sci. 1913, **79**, 132. F. P. 437397; abst. Mon. Sci. 1913, **79**, 134. F. P. 437804, 438248; abst. C. A. 1912, **6**, 3500; Mon. Sci. 1913, **79**, 135; Chem. Ztg. Rep. 1912, **36**, 514. F. P. 444044; abst. J. S. C. I. 1912, **31**, 1126; C. A. 1913, **7**, 1269; Mon. Sci. 1913, **79**, 142; Chem. Ztg. Rep. 1913, **37**, 35. F. P. 448511; abst. Mon. Sci. 1914, **81**, 4; J. S. C. I. 1913, **32**, 365. F. P. 466679; abst. J. S. C. I. 1914, **33**, 788. F. P. addn. 18568, 19228. F. P. 468349; abst. J. S. C. I. 1914, **33**, 962; Mon. Sci. 1916, **83**, 16. F. P. 473985; abst. J. S. C. I. 1915, **34**, 717; Mon. Sci. 1916, **83**, 81. F. P. 474023, 1914; abst. J. S. C. I. 1915, **34**, 716. D. R. P. 4472; abst. Wag. Jahr. 1879, **25**, 351. D. R. P. 13913, 34023; Wag. Jahr. 1886, **32**, 409. D. R. P. 45884, 158838; abst. Wag. Jahr. 1905, I, 500; Chem. Zts. 1905, **4**, No. 385; Zts. ang. Chem. 1905, **18**, 909. D. R. P. 162323; abst. Chem. Centr. 1905, **76**, II, 864; Chem. Ztg. 1905, **29**, 941; Jahr. Chem. 1905-1908, I, 1313; Zts. ang. Chem. 1905, **18**, 4781. D. R. P. 164382; abst. Chem. Ztg. 1905, **29**, 1328; Chem. Zts. 1906, **5**, No. 341; Wag. Jahr. 1905, I, 500; Zts. ang. Chem. 1906, **19**, 338. D. R. P. 167931; abst. Chem. Centr. 1906, I, 1384; Jahr. Chem. 1905-1908, I, 1319; Wag. Jahr. 1906, I, 579; Zts. ang. Chem. 1907, **20**, 325. D. R. P. 173620; abst. Chem. Centr. 1906, **77**, II, 935; Jahr. Chem. 1905-1908, I, 1312; Wag. Jahr. 1907, I, 589. D. R. P. 177519; abst. Chem. Centr. 1906, **77**, II, 1747; Jahr. Chem. 1905-1908, I, 1227; Wag. Jahr. 1907, I, 588. D. R. P. 179782; abst. Chem. Centr. 1907, I, 1470; Jahr. Chem. 1905-1908, I, 1317. D. R. P.

of the globe also contains this element in the ratio of something like 350 gm. per cubic meter. Assuming this crust to be 10 miles in depth, this roughly represents a weight of nitrogen of 179950; abst. Chem. Zentr. 1907, **78**, I, 1470; Jahr. Chem. 1905-1908, I, 1315; Wag. Jahr. 1907, I, 588. D. R. P. 180014; abst. Chem. Zentr. 1907, **78**, I, 1470; Jahr. Chem. 1905-1908, I, 1312; Wag. Jahr. 1907, I, 589. D. R. P. 183410; abst. Wag. Jahr. 1907, I, 589. D. R. P. 190958; abst. Chem. Zentr. 1908, I, 77; Jahr. Chem. 1905-1908, I, 1317; Wag. Jahr. 1907, I, 588. D. R. P. 191916; abst. Chem. Zentr. 1908, **79**, I, 566; Chem. Zts. 1908, **7**, No. 613; Jahr. Chem. 1905-1908, I, 1315; Wag. Jahr. 1908, I, 494. D. R. P. 193007; abst. Jahr. Chem. 1910, I, 406; Wag. Jahr. 1908, I, 494. D. R. P. 200053; abst. Chem. Zentr. 1908, **79**, II, 360; Wag. Jahr. 1908, I, 495. D. R. P. 201066; abst. Chem. Zentr. 1908, **79**, II, 739; Jahr. Chem. 1905-1908, I, 1319; Wag. Jahr. 1908, I, 586. D. R. P. 202778; abst. Chem. Zentr. 1908, **79**, II, 1754; Chem. Ztg. Rep. 1909, **33**, 11; Wag. Jahr. 1908, I, 495; Chem. Zts. 1908, **7**, No. 883; Jahr. Chem. 1905-1908, I, 1315. D. R. P. 203814; abst. Chem. Zentr. 1908, **79**, II, 1902; Chem. Ztg. Rep. 1909, **33**, 109; Jahr. Chem. 1905-1908, I, 1313; Wag. Jahr. 1909, I, 505. D. R. P. 204807; abst. Chem. Zentr. 1909, **80**, I, 478; Chem. Ztg. Rep. 1909, **33**, 138; Jahr. Chem. 1909, 374. D. R. P. 204882; abst. Mon. Sci. 1912, **77**, 50; Chem. Zentr. 1909, I, 323; Chem. Ztg. Rep. 1909, **33**, 12; Chem. Zts. 1909, **8**, No. 1087; Jahr. Chem. 1909, 511; Wag. Jahr. 1908, I, 492; Zts. ang. Chem. 1909, 457. D. R. P. 207425; abst. Chem. Zentr. 1909, I, 1284; Chem. Ztg. Rep. 1909, **33**, 266; Wag. Jahr. 1910, I, 125. D. R. P. 209848; abst. Mon. Sci. 1912, **77**, 167; Chem. Zentr. 1909, **80**, I, 1786; Chem. Ztg. Rep. 1909, **33**, 306; Jahr. Chem. 1909, I, 404. D. R. P. 220270; abst. Chem. Zentr. 1910, **81**, I, 1307; Chem. Ztg. Rep. 1910, **34**, 214; Jahr. Chem. 1910, I, 441; Wag. Jahr. 1910, I, 585. D. R. P. 222840; abst. Chem. Zentr. 1910, **81**, II, 256; Chem. Ztg. Rep. 1910, **34**, 350; Jahr. Chem. 1910, I, 442. D. R. P. 223064; abst. Chem. Zentr. 1910, **81**, II, 350; Chem. Ztg. Rep. 1910, **34**, 350; Jahr. Chem. 1910, I, 442. D. R. P. 223843; abst. Chem. Zentr. 1910, **81**, II, 520; Chem. Ztg. Rep. 1910, **34**, 415; Jahr. Chem. 1910, I, 442. D. R. P. 227100; abst. Chem. Zentr. 1910, **81**, II, 1347; Chem. Ztg. Rep. 1910, **34**, 551; Jahr. Chem. 1910, I, 412; Wag. Jahr. 1910, I, 571. D. R. P. 228487; abst. Chem. Zentr. 1910, **81**, II, 1728; Chem. Ztg. Rep. 1910, **34**, 611; Wag. Jahr. 1910, I, 406. D. R. P. 234849, 1910; abst. J. S. C. I. 1911, **30**, 895. D. R. P. 240837; abst. C. A. 1912, **6**, 2061; Chem. Ztg. Rep. 1911, **35**, 628; Wag. Jahr. 1911, I, 201. D. R. P. 241464; abst. C. A. 1912, **6**, 2062; Chem. Ztg. Rep. 1912, **36**, 15; Wag. Jahr. 1912, I, 200; Zts. ang. Chem. 1912, **25**, 130. D. R. P. 246341; abst. C. A. 1912, **6**, 2345; Chem. Ztg. Rep. 1912, **36**, 303; Wag. Jahr. 1912, I, 512; Zts. ang. Chem. 1912, **25**, 1140. D. R. P. 249856; abst. C. A. 1912, **6**, 3170; Chem. Zentr. 1912, **83**, II, 651; Chem. Ztg. Rep. 1912, **36**, 481; Wag. Jahr. 1912, I, 509; Zts. ang. Chem. 1912, **25**, 1929. D. R. P. 255488; abst. C. A. 1913, **7**, 1959; Chem. Zentr. 1913, **84**, I, 479; Chem. Ztg. Rep. 1913, **37**, 79; Wag. Jahr. 1913, I, 534; Zts. ang. Chem. 1913, **26**, 106. D. R. P. 259877; abst. J. S. C. I. 1913, **32**, 699; C. A. 1913, **7**, 3205; Chem. Zentr. 1913, II, 107; Chem. Ztg. Rep. 1913, **37**, 320; Wag. Jahr. 1913, I, 535; Zts. ang. Chem. 1913, **26**, 382. D. R. P. 260758; abst. C. A. 1913, **7**, 3206; Chem. Zentr. 1913, **84**, I, 195; Chem. Ztg. Rep. 1913, **37**, 372; Wag. Jahr. 1913, I, 535; Zts. ang. Chem. 1913, **26**, 412. D. R. P. 260948; abst. C. A. 1913, **7**, 3053; Chem. Zentr. 1913, **84**, I, 195; Chem. Ztg. Rep. 1913, **37**, 385; Wag. Jahr. 1913, I, 535. D. R. P. 261735; abst. C. A. 1913, **7**, 3645; Chem. Zentr. 1913, **84**, I, 325; Chem. Ztg. Rep. 1913, **37**, 448; Wag. Jahr. 1913, I, 530; Zts. ang. Chem. 1913, **26**, 462. D. R. P. 262728; abst. C. A. 1913, **7**, 3822; Chem. Zentr. 1913, **84**, II, 730; Chem. Ztg. Rep. 1913, **37**, 476; Wag. Jahr. 1913, I, 536; Zts. ang. Chem. 1913, **26**, 518. Aust. P. 49226; same as D. R. P. 204882; abst. Mon.

about 4.5 tons per square yard of surface. Someone has computed there are 20,000,000 tons of nitrogen above each square mile of the earth, which is an amount equivalent to the demands of the world for the past 75 years. It has been estimated that only about two parts in a million of this vast amount is in actual use, the balance being present as an unassimilable reserve.

Separation of Nitrogen from the Air. T. Lowry¹ has described an unstable oxidizable modification of nitrogen obtainable by electric sparking through air which is oxidized to nitrogen by ozone. C. Blagburn² obtains nitrogen by directing the whole of a stream of air into contact with an excess of sulfur, at not less than the temperature of ignition, and removing from the N

Sci. 1912, **77**, 50; Chem. Zentr. 1909, **89**, I, 323; Chem. Ztg. Rep. 1909, **33**, 12; Chem. Zts. 1909, **8**, No. 1087; Jahr. Chem. 1909, **62**, 511; Wag. Jahr. 1908, I, 492; Zts. ang. Chem. 1909, **22**, 457; Swiss P. 42515, 51110, 56840, 59117, 64235, 67705. For the manufacture of nitrogen and nitric acid, compare: Norw. P. 10167, 12684, 12689, 13925, 14102, 14209, 14830, 14885, 14975, 15021, 15369, 16042, 16045, 16083, 16203, 16512, 17193, 17257, 17644, 18030, 18031, 19124, 19262, 19343, 19399, 20045, 20407; abst. Mon. Sci. 1906, **65**, 74; 1907, **67**, 81; 1908, **69**, 108, 109; 1911, **75**, 81, 82; 1913, **79**, 90; 1914, **81**, 81; Chem. Ztg. 1905, **29**, 457, 825; 1906, **30**, 224, 401; Chem. Ztg. Rep. 1907, **31**, 207, 242; 1908, **32**, 552; 1910, **34**, 259. Norw. P. 20487, 20797, 21930, 22163, 22183, 22208, 22498, 22583, 22740, 22803, 22894; abst. C. A. 1913, **7**, 2289. 23041, 23152, 23362, 23420, 23575; abst. C. A. 1914, **8**, 796. See also Allgemeine Elektrizitäts Ges. E. P. 8426, 1908; abst. C. A. 1910, **4**, 91. Elektrochem. Werke and F. Rothe, D. R. P. 261027, 1911; abst. C. A. 1913, **7**, 3207. Manuelli, L'engrais, **24**, 887; abst. C. N. 1886, **53**, 151. G. Ireland and H. St. Sugden, D. R. P. 175401; abst. Mon. Sci. 1908, **69**, 153; Chem. Zentr. 1906, **77**, II, 1118; Chem. Ztg. Rep. 1906, **30**, 325; Chem. Zts. 1907, **6**, 19, 78, Jahr. Chem. 1905-1908, I, 1693, 1694; Wag. Jahr. 1906, I, 403; Zts. ang. Chem. 1907, **20**, 972; Zts. Schiess. Spreng. 1906, **1**, 390. 176616; abst. Mon. Sci. 1909, **71**, 65; Chem. Zentr. 1907, **78**, I, 1162; Chem. Ztg. Rep. 1907, **31**, 34; Chem. Zts. 1907, **6**, 78, No. 1; Jahr. Chem. 1905-1908, I, 1693; Wag. Jahr. 1906, I, 404; Zts. ang. Chem. 1907, **20**, 1376. 180141; abst. Mon. Sci. 1909, **71**, 65; Chem. Zentr. 1907, **78**, I, 1163; Chem. Ztg. Rep. 1907, **31**, 48; Jahr. Chem. 1905-1908, I, 1694; Wag. Jahr. 1907, I, 350; Zts. ang. Chem. 1907, **20**, 1376; Zts. Schiess. Spreng. 1907, **2**, 35. H. Woltereck, D. R. P. 146712; abst. Mon. Sci. 1904, **61**, 82; Chem. Zentr. 1903, **74**, II, 1264; Chem. Ztg. 1903, **27**, 1158; Chem. Zts. 1904, **3**, 337; Jahr. Chem. 1903, **56**, 365; Wag. Jahr. 1903, I, 280; Zts. ang. Chem. 1903, **16**, 1160. G. Jones and P. Suarez, D. R. P. 220670; abst. Mon. Sci. 1914, **81**, 76; Chem. Zentr. 1910, **81**, I, 1470; Chem. Ztg. Rep. 1910, **34**, 179; Jahr. Chem. 1910, I, 553; Wag. Jahr. 1910, I, 427; Zts. ang. Chem. 1910, **23**, 6049. D. R. P. 234793; abst. Chem. Zentr. 1911, **82**, I, 1726; Chem. Ztg. Rep. 1911, **35**, 303; Wag. Jahr. 1911, I, 430; Zts. ang. Chem. 1911, **24**, 1193.

1. Phil. Mag. 1914, (6), **28**, 112; Trans. Faraday Soc. 1914, **9**, 189; J. S. C. I. 1914, **33**, 961.

2. E. P. 25535, 1908; abst. C. A. 1910, **4**, 91; J. S. C. I. 1909, **28**, 794; L'engrais, **24**, 914; abst. C. A. 1910, **4**, 88. Meister, Lucius & Bruening, Swiss P. 64235, and addn. 68919, 1914. G. Roettger, Belg. P. 224544, 1910. J. Wallace and E. Wassmer, Swiss P. 62845, 1912; abst. C. A. 1914, **8**, 2232.

the oxygen compounds of sulfur. The process of C. Acker¹ consists in passing dry air and CO₂ over molten sodium cyanide forming the cyanate and leaving the N free for collection. H. Blau separates O and N from air by liquefaction and condensation, employing the O boiling under a lower pressure than the gaseous mixture in the column for the reflux condensation of the N in the upper end of the column.² Or,³ fractional distillation of the liquified O and N may be used for separation. The Ashcroft process⁴ is similar.

The heated air may also be led over finely divided copper,⁵ molten lead,⁶ potassium,⁷ cupric oxide,⁸ silica with lime, barium oxide or magnesite,⁹ alkaline plumbates or manganates,¹⁰ phos-

1. Can. P. 132714, 1911; abst. C. A. 1911, **5**, 2921; abst. Mon. Sci. 1912, **77**, 17. See also Nitrogen Co., E. P. 24413, 1910; abst. C. A. 1911, **5**, 3135. D. R. P. 258295, 1910; abst. C. A. 1913, **7**, 2999; Chem. Zentr. 1913, I, **84**, 1479; abst. Chem. Ztg. Rep. 1913, **37**, 257; abst. Wag. Jahr. 1913, I, **59**, 537. E. Ashcroft, U. S. P. 1320192, 1919; abst. C. A. 1920, **14**, 102. O. Hurford, Swiss P. 52711, 1910. G. Kaszner, Aust. P. 53023, 1912; 58959, 1913.

2. D. R. P. 223843, 1909; abst. C. A. 1910, **4**, 3287; abst. Chem. Zentr. 1910, **81**, II, 520; abst. Chem. Ztg. Rep. 1910, **34**, 415; abst. Jahr. Chem. 1910, I, **63**, 442. J. Island, U. S. P. 1117705, 1919; abst. J. S. C. I. 1919, **38**, 900-A. L. Nevens, Belg. P. 240076, 1911. F. Slocum, U. S. P. 1318929, 1919; abst. C. A. 1920, **14**, 102. E. P. 133104, 1918; abst. J. S. C. I. 1919, **38**, 900-A, 946-A.

3. L'air Liquid Soc. Anon. Pour L'Etude et L'Exploitation des Procédés Geogres Claude & René J. Levy, D. R. P. 202778, 1904; abst. C. A. 1909, **3**, 696; Chem. Zentr. 1908, **79**, II, 1754; Chem. Ztg. Rep. 1909, **33**, 11; Chem. Zts. 1908, **7**, No. 883; Jahr. Chem. 1905-1908, I, 1315. Belg. P. 198051, 200735, 203784, 1907; 224191, 1910. E. Haslup, E. P. 134885, 135889. U. S. P. 1310478; abst. J. S. C. I. 1919, **38**, 629-A; 1920, **39**, 23-A.

4. E. P. Appl. 6382, 6383, 1918; abst. J. S. C. I. 1918, **37**, 258-A.

5. Cyanid-Ges., D. R. P. 218671, 1908; abst. C. A. 1910, **4**, 1797; Chem. Zentr. 1910, **81**, I, 781; Chem. Ztg. Rep. 1910, **34**, 107; Jahr. Chem. 1910, **63**, I, 548; Zts. ang. Chem. 1910, **23**, 762; Zts. Schiess. Spreng. 1910, **5**, 114. See C. Bradley and D. Lovejoy, U. S. P. 709867, 709868, 1902; abst. J. S. C. I. 1902, **21**, 1335; Chem. Ztg. 1902, **26**, 1018. Atmospheric Products Co., E. P. 8230, 1901; abst. J. S. C. I. 1901, **20**, 726. C. Bradley, U. S. P. 1134583; abst. J. S. C. I. 1915, **34**, 552. A. Crowell, U. S. P. 1321892; abst. J. S. C. I. 1920, **39**, 21-A. Bergmann Elektrizitäts Werke, D. R. P. 298952, 1916; abst. J. S. C. I. 1920, **39**, 21-A.

6. C. Acker, U. S. P. 1050902, 1913; abst. C. A. 1913, **7**, 871; Mon. Sci. 1913, **79**, 100; Chem. Ztg. Rep. 1913, **37**, 379.

7. Nitrogen Co., E. P. 24413, 1910; abst. J. S. C. I. 1911, **30**, 621.

8. A. Frank, D. R. P. 204882, 1907; abst. C. A. 1909, **3**, 1449; Mon. Sci. 1912, **77**, 60; Chem. Zentr. 1909, **80**, I, 323; Chem. Ztg. Rep. 1909, **33**, 12; Chem. Zts. 1909, **8**, No. 1087; Jahr. Chem. 1909, **62**, 511; Wag. Jahr. 1908, **54**, I, 492; Zts. ang. Chem. 1909, **22**, 457. E. P. 16963, 1908; abst. C. A. 1909, **3**, 3000; J. S. C. I. 1909, **28**, 939.

9. O. Frank, E. P. 1774, 1912; abst. C. A. 1913, **7**, 2456.

10. G. Kassner, U. S. P. 1015566, 1912; abst. C. A. 1912, **6**, 796; Mon. Sci. 1912, **77**, 131. E. P. 12307, 12308, 1911; abst. C. A. 1912, **6**, 3169; J. S. C. I. 1911, **30**, 1314, 1383. F. P. 430093, 1911; abst. C. A. 1912, **6**, 2149;

phorus,¹ other molten metal,² or by burning carbonaceous fuel in an enclosed space,³ the general idea being to combine the oxygen, thus leaving the nitrogen substantially pure.

The separation of these two elements by combinations of heat and pressure with selective fractionation of the O from the N form the basis of the described processes of R. Pictet,⁴ E. Wiley,⁵ G. Roettger,⁶ J. Lilienfeld,⁷ A. Melville,⁸ Barbet et Fils et Cie,⁹ O. Frank and O. Fincke,¹⁰ G. Jakova-Merturi¹¹ and the Ges. Lindes Eismaschinen A. G.¹² The apparatus of O. Rast¹³ for the production of N depends upon the solubility of O in water.

Mon. Sci. 1913, **79**, 127; Chem. Ztg. Rep. 1912, **36**, 59. D. R. P. 233383, 1910; abst. C. A. 1911, **5**, 2710; Chem. Zentr. 1911, **82**, I, 1261; Chem. Ztg. Rep. 1911, **35**, 210; Wag. Jahr. 1911, **57**, I, 356; Zts. ang. Chem. 1911, **24**, 856. D. R. P. 237232, 1910; addn. to D. R. P. 233383, 1910; abst. C. A. 1912, **6**, 1507; Chem. Zentr. 1911, **82**, II, 497; Chem. Ztg. Rep. 1911, **35**, 470; Wag. Jahr. 1911, **57**, I, 542; Zts. ang. Chem. 1911, **24**, 1657.

1. R. Wallace and E. Wassmer, U. S. P. 1154145, 1915; abst. C. A. 1915, **9**, 3119. E. P. 14631, 1911; 3147, 1912; abst. C. A. 1913, **7**, 222, 2457; Chem. Ztg. Rep. 1912, **37**, 33.

2. W. Heys, E. P. 17666, 1911; abst. C. A. 1913, **7**, 403; J. S. C. I. 1912, **31**, 129.

3. O. Hurford, E. P. 19402, 1908; abst. C. A. 1910, **4**, 816; J. S. C. I. 1909, **28**, 1088. For "active" nitrogen, see R. Strutt, Proc. Roy. Soc. 1911, **85**, A, 219; **86**, A, 56; 1913, **88**, A, 539; 1915, **91**, A, 303; 1916, **92**, A, 438; abst. J. S. C. I. 1911, **30**, 683; 1912, **31**, 70; 1913, **32**, 750; 1915, **34**, 422; 1916, **35**, 837. W. Jevons, Proc. Roy. Soc. 1915, **91**, A, 120; abst. J. S. C. I. 1915, **34**, 175.

4. E. P. 27463, 1910; abst. C. A. 1911, **5**, 3329; J. Soc. Dyers Col. 1911, **30**, 804. J. Bucher, U. S. P. 1091425, 1138191. E. P. 455799; abst. J. S. C. I. 1913, **32**, 943; 1915, **34**, 661; C. A. 1914, **8**, 1860, 1856; Mon. Sci. 1914, **80**, 12; Chem. Ztg. Rep. 1914, **38**, 39, 467; Zts. ang. Chem. 1916, **29**, I, 134.

5. U. S. P. 1056244, 1915; abst. C. A. 1913, **7**, 1589; Chem. Ztg. Rep. 1913, **37**, 464.

6. E. P. 7858, 1910; abst. C. A. 1911, **5**, 2918; J. S. C. I. 1911, **30**, 27; Chem. Ztg. Rep. 1911, **35**, 471.

7. D. R. P. 255488, 1910; abst. C. A. 1913, **7**, 1959; Chem. Zentr. 1913, **84**, I, 481; Chem. Ztg. Rep. 1913, **37**, 79; Wag. Jahr. 1913, **59**, I, 534; Zts. ang. Chem. 1913, **26**, 106.

8. Aust. P. 34567, 34568.

9. E. P. 131321, 1918; abst. J. S. C. I. 1918, **37**, 78-A; 1919, **38**, 700, 766-A. F. P. Jan. 31, 1917. See also "Rectification de l'air liquide," E. Barbet, 1918, 139 p.

10. E. P. 10718, 1912; abst. C. A. 1913, **7**, 3534; J. S. C. I. 1912, **31**, 1032.

11. F. P. 482668, 1917; abst. C. A. 1918, **12**, 208; Mon. Sci. 1918, **84**, 44.

12. D. R. P. 203814, 1906; abst. Chem. Zentr. 1908, **79**, II, 1902; Chem. Ztg. Rep. 1909, **33**, 109; Jahr. Chem. 1905-1908, I, 1313; Wag. Jahr. 1909, **55**, I, 505.

13. D. R. P. 253494, 1911; abst. C. A. 1913, **7**, 813; Chem. Zentr. 1912, **83**, II, 1953; Chem. Ztg. Rep. 1912, **36**, 670; Wag. Jahr. 1912, I, **58**, 505; Zts. ang. Chem. 1912, **25**, 2608.

R. Levy and A. Helbronner¹ separate O from N by liquefaction, rectification, re-liquefaction of the gas rich in N, and further purification.

The Industriegas-Ges. fuer Sauerstoff und Stickstoff-Anlagen² produce N from liquid air by leading it counter to a rising current of O, whereby heat is introduced from without in such a manner that the N separates from the liquid air from the heating vapors by impermeable walls. Or³ the air may be caused to pass in succession through two tubular systems, in which the second system and the upper portion of the first are maintained at a lower temperature than that of the lower part of the first. T. Briggs,⁴ P. Guye⁵ and Pease⁶ have also contributed to the sub-

1. U. S. P. 959563, 1910; abst. C. A. 1910, **4**, 2539; Mon. Sci. 1910, **73**, 130. See also Anon., Chem. Ind. 1910, **33**, 725; abst. C. A. 1911, **5**, 1169.

2. F. P. 446560, 1912; abst. C. A. 1913, **7**, 1958; Chem. Ztg. Rep. 1913, **37**, 96. D. R. P. 312639, 1913; abst. J. S. C. I. 1919, **38**, 862-A.

3. Soc. L'Air Liquide, E. P. 7175, 1910; abst. C. A. 1911, **5**, 2159; J. S. C. I. 1910, **29**, 1011. E. P. 7305, 1910; abst. C. A. 1911, **5**, 2918; J. S. C. I. 1910, **29**, 1251. F. P. 488444, 1917.

4. Electrochem. Met. Ind. **5**, 485. See also Mosicki, Electrochem. Met. Ind. **5**, 491.

5. Schweiz. Chem. Zts. 1918, **2**, 3; abst. J. S. C. I. 1918, **37**, 179-A. For equilibrium constants in the Bucher process for nitrogen fixation, see J. Ferguson and P. Manning, J. Ind. Eng. Chem. 1919, **11**, 946; abst. J. S. C. I. 1920, **39**, 17-A.

6. E. P. Appl. 1453, 1918; abst. J. S. C. I. 1918, **37**, 79-A. For additional data on the separation of nitrogen from the air, compare C. Andreucci, E. P. 117333, 1917; U. S. P. 1272181, 1918; Cf. E. P. 16277-A, 1896; abst. J. S. C. I. 1917, **36**, 83; 1918, **37**, 507-A; C. A. 1918, **12**, 2417, 1915. Atmospheric Oxygen and Power Co., E. P. 321860, 1902; abst. J. S. C. I. 1903, **22**, 208. J. Currie, U. S. P. 1263533, 1918; abst. C. A. 1918, **12**, 121, 1618. Cowper-Coles, E. P. Appl. 13886, 1918; abst. J. S. C. I. 1918, **37**, 535-A. G. Claude, U. S. P. 1025962, 1912, 1068210, 1913; E. P. 3226, 1911; F. P. 403777, 1908; abst. J. S. C. I. 1910, **29**, 88; 1912, **31**, 335, 588; 1913, **32**, 827. Ges. fur Linde's Eismaschinen A.-G., E. P. 109789, 1917; addn. to E. P. 24735, 1914; abst. J. S. C. I. 1918, **37**, 507-A, 1915, **34**, 871. G. Hildebrandt, U. S. P. 1119158, 1119159, 1914; abst. J. S. C. I. 1915, **34**, 80. W. Hoofnagle, U. S. P. 1243524, 1917; abst. J. S. C. I. 1917, **36**, 127. M. Hazard-Flamand, U. S. P. 1201043, 1201044, 1916; F. P. 394881, 1907; abst. J. S. C. I. 1909, **28**, 310; 1916, **35**, 1156. G. James, W. Vint and H. Alexander, E. P. 117937, 1917; abst. J. S. C. I. 1918, **37**, 581-A. G. Jaubert, E. P. 440702, 1911; 465822, 1913; abst. J. S. C. I. 1912, **31**, 875; 1914, **33**, 645. K. Kaiser, E. P. 435397, 1911; abst. J. S. C. I. 1912, **31**, 385. C. Krapf, U. S. P. 1212504, 1917; F. P. 464750, 1913; abst. J. S. C. I. 1917, **36**, 339; 1914, **33**, 549. J. Lilienfeld, E. P. 22930, 1911; F. P. 435357, 1911; abst. J. S. C. I. 1912, **31**, 385, 1079. R. Levy and A. Helbronner, E. P. 328770, 328984, 1903; abst. J. S. C. I. 1903, **22**, 996. Montgomery and Royston, E. P. Appl. 9210, 1916; abst. J. S. C. I. 1916, **35**, 43. E. Maxted and T. Smith, E. P. 114663, 1917; abst. J. S. C. I. 1918, **37**, 302-A. J. Place, E. P. 105106, 1916; U. S. P. 707633; 707634, 1902; 1157959, 1915; abst. J. S. C. I. 1902, **21**, 1322; 1915, **34**, 1209; 1917, **36**, 548. R. Pictet, E. P. 457031, 1912, and first addn. 1913, 322000,

ject of the separation and purification of elemental nitrogen.

Other methods for obtaining purified nitrogen have been described by Elektrizitätswerk Lonza,¹ R. Williams,² J. Mai,³ O. v. Knorre,⁴ N. Bacon,⁵ N. Tommassi,⁶ W. Mount,⁷ H. Rai,⁸ Messer & Co.,⁹ M. Should,¹⁰ Harger and Lever Bros.,¹¹ C. McCourt, and C. Ellis,¹² Montgomery and Royston,¹³ and C. Crommett.¹⁴

Among the factory methods for the preparation of this element in a pure state may be mentioned the process of the Nitro-

1902; E. P. 2713, 1901; abst. J. S. C. I. 1902, **21**, 407; 1903, **22**, 364; 1913, **32**, 1108, 1109. C. Rossi, U. S. P. 1266717, 1918; abst. C. A. 1918, **12**, 1733. Slocum, E. P. Appl. 4451, 1918; abst. J. S. C. I. 1918, **37**, 171-A. Soc. Anon. pour l'Étude et l'Exploit. des proc. G. Claude, E. P. 12905, 1900; 3326, 1911; 114817, 1917; F. P. 296211, 1900; 321097, 324460, 1902; 328245, 1903; abst. J. S. C. I. 1901, **20**, 1018; 1903, **22**, 298, 485, 554, 796, 950; 1912, **31**, 335; 1918, **37**, 416-A. E. Wiley, U. S. P. 1056244, 1913; abst. J. S. C. I. 1913, **32**, 426.

1. E. P. 127852, 1917; abst. J. S. C. I. 1919, **38**, 537-A. D. R. P. 302671, 1916; abst. J. S. C. I. 1918, **37**, 335-A.

2. U. S. P. 1314231, 1919; abst. J. S. C. I. 1919, **38**, 765-A. A. Lynn, E. P. 3194, 1913; abst. J. S. C. I. 1914, **33**, 352; C. A. 1914, **8**, 2926; Chem. Ztg. Rep. 1914, **38**, 230.

3. Ber. 1901, **34**, 3805; abst. J. S. C. I. 1902, **21**, 76. C. Monreau and A. Lepape, Compt. rend. 1914, **158**, 839; abst. J. S. C. I. 1914, **33**, 1118.

4. Chem. Ztg. 1903, **27**, 550; abst. J. S. C. I. 1903, **22**, 795. C. Van Brunt, J. A. C. S. 1914, **36**, 1148; abst. J. S. C. I. 1914, **33**, 788.

5. U. S. P. 1304932, 1919; abst. J. S. C. I. 1919, **38**, 577-A; C. A. 1919, **13**, 2113. T. Lowry, Proc. Chem. Soc. 1912, **28**, 64; abst. J. S. C. I. 1912, **31**, 383.

6. U. S. P. 1295635, 1919; abst. J. S. C. I. 1919, **38**, 321-A; C. A. 1919, **13**, 1248. D. R. P. 302671, 1916; abst. J. S. C. I. 1918, **37**, 335-A. Can. P. 185847; abst. C. A. 1919, **13**, 2045.

7. U. S. P. 1304796, 1919; abst. C. A. 1919, **13**, 1960. R. Brandt, Zts. ang. Chem. 1914, **27**, 424; abst. J. S. C. I. 1914, **33**, 749.

8. J. S. C. I. 1919, **38**, 99-R; abst. C. A. 1919, **13**, 3087. W. Adeney and H. Becker, Sci. Proc. Roy. Dublin Soc. 1918, **15**, 385; abst. J. S. C. I. 1919, **38**, 156-A. See also E. P. 322600, 328245, 332662, 338064, 322600 and addn. 2277, 332811; addn. 4007 to 328245, 352254, 372099, 410933, 410967, 423328, 430060, 430093.

9. D. R. P. 300041, 1914; abst. J. S. C. I. 1919, **38**, 861-A. J. Collie, H. Patterson and I. Masson, C. A. 1915, **9**, 20.

10. U. S. P. 1287472, 1918; abst. J. S. C. I. 1919, **38**, 135-A. E. Rutherford, C. A. 1919, **13**, 2480.

11. E. P. 131684, 1919; abst. J. S. C. I. 1919, **38**, 700-A. M. Born, Ber. Physik. Ges. 1917, **19**, 243; 1918, **20**, 16; abst. C. A. 1919, **13**, 1421.

12. U. S. P. 1289496, 1918; abst. J. S. C. I. 1919, **38**, 136-A. E. P. 25629, 1912; abst. J. S. C. I. 1913, **32**, 751. H. Collins, Chem. News, 1919, **119**, 29; abst. C. A. 1919, **13**, 3065. In this connection see C. A. 1908, **2**, 3; 1911, **5**, 3756; 1913, **7**, 1831; 1914, **8**, 864, 1362.

13. E. P. 131609, 1919; abst. J. S. C. I. 1919, **38**, 700-A. F. Loring, Chem. News, 1919, **118**, 311; abst. C. A. 1919, **13**, 2482.

14. U. S. P. 1304027, 1919; abst. C. A. 1919, **38**, 2113. F. Briner and P. Naville, Helvetica Chim. Acta, 1919, **2**, 3482; abst. C. A. 1919, **13**, 2487.

gen Co.,¹ and that of Parkes and Pearson.² J. Currie³ arranges in alignment two electrodes having relatively wide, flat, annular opposed, parallel arcing surfaces, so that a relatively thick arc may be produced. The electrodes are water-cooled, internally and externally. For nitrogen fixation apparatus, silicon,⁴ nickel-chromium-copper alloy,⁵ powdered tantalum,⁶ or molten sulfur⁷ have been the basis of patent protection.

A. Frank and N. Caro⁸ pass fuel gases over a metal containing its oxide whereby the carbon monoxide and the hydrocarbons are burned to CO₂, which is afterwards removed by absorption; R. Meves⁹ obtains pure N by liquefying air by the Linde process, and fractional distillation of the liquid air, or by repeatedly compressing air up to its liquefaction point, pure nitrogen remaining,¹⁰ the G. Jaubert apparatus being used.¹¹ T. Willson and M. Haff¹² burn sulfur in a limited quantity of air, pass the mixture of O, N and SO₂ thus formed through milk of lime, and the N over heated S, absorbing SO₂ and leaving the nitrogen in a pure state.

1. F. P. 423462, 1910; abst. C. A. 1912, **6**, 1969; Mon. Sci. 1913, **79**, 117; Chem. Ztg. Rep. 1911, **35**, 306; D. R. P. 260804, abst. C. A. 1913, **7**, 3206; Chem. Zentr. 1913, **84**, 11, 187; Chem. Ztg. Rep. 1913, **37**, 385; Wag. Jahr. 1913, **59**, I, 515; Zts. ang. Chem. 1913, **26**, 437.
2. E. P. Appl. 4623, 1918; abst. J. S. C. I. 1918, **37**, 1704.
3. Can. P. 174360, 1917; abst. C. A. 1918, **12**, 121. E. Ashcroft, E. P. 10420, 1914; 125714; C. A. 1919, **13**, 2263; abst. J. S. C. I. 1915, **34**, 716. U. S. P. 1186367; abst. J. S. C. I. 1915, **34**, 716; 1916, **35**, 840; Chem. Ztg. Rep. 1917, **41**, 124.
4. O. Frank, E. P. 1774, 1912; abst. C. A. 1913, **7**, 2456.
5. R. McKee, U. S. P. 1236853, 1917; abst. C. A. 1917, **11**, 2948; J. S. C. I. 1917, **35**, 1048.
6. Siemens & Halske, D. R. P. 286514; abst. J. S. C. I. 1916, **35**, 48; Mon. Sci. 1918, **84**, 18; Chem. Zentr. 1915, **86**, 11, 564; Chem. Ztg. Rep. 1915, **39**, 378; Zts. ang. Chem. 1915, **28**, 471.
7. C. Blagburn, E. P. 25535, 1908; abst. C. A. 1910, **4**, 91; J. S. C. I. 1909, **28**, 794.
8. D. R. P. 204882; abst. Chem. Zts. 1909, **8**, 1087; Mon. Sci. 1912, **77**, 50; Wag. Jahr. 1908, **54**, I, 492; Chem. Zentr. 1909, **80**, I, 323; Chem. Ztg. Rep. 1909, **33**, 12; Zts. ang. Chem. 1909, **22**, 457; Jahr. Chem. 1909, **62**, 511. In this connection see O. Serpek, D. R. P. 181991, 183702; abst. Mon. Sci. 1909, **71**, 153; Chem. Zentr. 1907, **78**, I, 1520; II, 651; Chem. Ztg. Rep. 1907, **31**, 136, 207; Jahr. Chem. 1905-1908, I, 2541; Wag. Jahr. 1907, **53**, I, 449, 450; Zts. ang. Chem. 1907, **20**, 1376; 1908, **21**, 790.
9. D. R. P. 179782; abst. Chem. Zentr. 1907, **78**, I, 1470; Jahr. Chem. 1905-1908, I, 1317.
10. A. Neumann, D. R. P. 281518; abst. Chem. Zentr. 1915, **86**, I, 281; Chem. Ztg. Rep. 1915, **39**, 40; C. A. 1915, **9**, 1863; Zts. ang. Chem. 1915, **28**, 80.
11. D. R. P. 277717; abst. Chem. Ztg. Rep. 1914, **38**, 511; Wag. Jahr. 1914, **60**, I, 436; Zts. ang. Chem. 1914, **27**, 620.
12. U. S. P. 1084774; abst. C. A. 1914, **8**, 995; Chem. Ztg. Rep. 1914, **38**, 237; Zts. ang. Chem. 1915, **28**, 223.

In another method,¹ liquids are employed which dissolve O more readily than N.

G. Weiboeck² absorbs the O by means of fresh, moist bark;² R. Wallace and E. Wassmer³ pass air over phosphorus and separate the products in an intricate manner,³ the methods of Hurford,⁴ Nitrogen Gesellschaft⁵ and E. and J. Behrens⁶ being analogous. O. Hurford⁷ first burns a carbonaceous fuel in sufficient air to form CO₂, then separating the N therefrom by means of the condensing action of water.

For the separation of the nitrogen from the oxygen in the air, H. Barsehall⁸ employs two rectifying columns, one above the other, from which the O is taken away at the bottom and the N at the top. A similar apparatus⁹ separates the N from O in the air by liquefaction, brought about by compression, countercurrent cooling, and expansion and fractionation by partial re-evaporation.

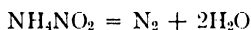
L. Summers,¹⁰ E. Scott,¹¹ A. Sander,¹² A. Hooker,¹³ O. Austin,¹⁴

1. Salpetersaure Industrie Ges., D. R. P. 182849; abst. Mon. Sci. 1911, **75**, 15; Chem. Zentr. 1907, **78**, II, 651; Chem. Ztg. Rep. 1907, **31**, 168; Jahr. Chem. 1905-1908, I, 1766; Wag. Jahr. 1907, **53**, I, 482. Brunler, D. R. P. 204730; abst. Chem. Zentr. 1909, **81**, I, 323; Chem. Ztg. Rep. 1909, **33**, 11; Chem. Zts. 1909, **8**, No. 1113; Jahr. Chem. 1909, **62**, 397; Wag. Jahr. 1908, **54**, I, 493; Zts. ang. Chem. 1909, **22**, 458.
2. D. R. P. 193410; abst. Chem. Zentr. 1908, **79**, I, 906; Chem. Ztg. Rep. 1908, **32**, 80; Chem. Zts. 1908, **7**, No. 619; Jahr. Chem. 1905-1908, I, 1319; Wag. Jahr. 1908, **54**, I, 495; Zts. ang. Chem. 1908, **21**, 800.
3. E. P. 3147, 1912; abst. C. A. 1913, **7**, 2457; J. S. C. I. 1913, **32**, 364; Chem. Ztg. Rep. 1913, **37**, 476.
4. U. S. P. 914279, 1909; abst. C. A. 1909, **3**, 1447; Chem. Ztg. Rep. 1909, **33**, 208.
5. F. P. 468349; abst. Mon. Sci. 1916, **83**, 16; D. R. P. 215608; abst. Mon. Sci. 1913, **79**, 65; Chem. Zentr. 1909, **80**, II, 1708; Chem. Ztg. Rep. 1909, **33**, 592; Jahr. Chem. 1909, **62**, I, 511; Wag. Jahr. 1909, **55**, I, 499; Zts. ang. Chem. 1909, **22**, 2434.
6. D. R. P. 226942; abst. Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1910, **81**, II, 1345; Chem. Ztg. Rep. 1910, **34**, 551; Jahr. Chem. 1910, **63**, I, 633; Wag. Jahr. 1910, **56**, I, 561; Zts. ang. Chem. 1910, **23**, 2337.
7. E. P. 19492, 1908; abst. C. A. 1910, **4**, 816; J. S. C. I. 1909, **28**, 1088.
8. D. R. P. 259877, 1911; abst. C. A. 1913, **7**, 3205; Chem. Ztg. Rep. 1913, **37**, 320; Wag. Jahr. 1913, **59**, I, 535; Zts. ang. Chem. 1913, **26**, 382.
9. Industriegas-Ges. für Sauerstoff und Stickstoffanlagen, D. R. P. Anm. J. 13634.
10. Proc. Am. Inst. Elec. Eng. March, 1915.
11. Elec. Eng. (N. Y.) 1917, **50**, 45; abst. C. A. 1918, **12**, 252.
12. Zts. Komp. fluss. Gase. 1915, **17**, 1; abst. C. A. 1916, **10**, 1696.
13. Trans. Am. Electrochem. **29** (advanced copy); Met. Chem. Eng. 1916, **14**, 261; J. Ind. Eng. Chem. 1916, **8**, 288; C. A. 1916, **10**, 852.
14. The Americas, 1918, **4**, 21; abst. C. A. 1918, **12**, 1269.

P. Guye,¹ H. Prinsengeerligs,² R. Skerrett,³ F. Carpenter,⁴ and others⁵ have given historical and detailed reviews of the various phases of this subject.

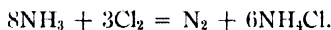
Preparation of Pure Nitrogen. This cannot readily be prepared from the air due to the presence of elements of the helium group, it, however, may be prepared from nitrogen compounds, as in the following five ways:

(1) The following reaction takes place when a concentrated solution of ammonium nitrite is heated:

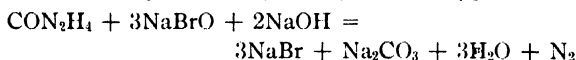


It is more convenient to employ stoichiometrical quantities of sodium nitrite and ammonium sulfate.

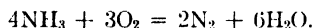
(2) The action of chlorine upon ammonia gives pure nitrogen:



(3) Urea may be decomposed by alkaline hypobromite:



(4) Pass a mixture of ammonia and oxygen through a heated tube containing iron or copper



(5) Nitrous oxide or nitric oxide is passed over heated copper or iron



The action of sulfuric acid upon a mixture of ammonium nitrite and glycerol also produces nitrogen. In addition there are many methods in which oxygen is removed from the air, as indicated in the next topic.

Properties of Nitrogen. Pure nitrogen is a colorless, odorless gas, ordinarily inactive, a non-supporter of combustion, and directly combining with but very few metals. Indirectly it combines to form many compounds as nitric acid—in connection with the subjects treated in this series of volumes—of far-reach-

1. J. suisse de Chimie. L'Industrie Chim. 1918, **5**, ii; abst. C. A. 1918, **12**, 1498.

2. Louisiana Planter, 1915, **54**, 347; abst. C. A. 1915, **9**, 2429.

3. Iron Age, 1916, **97**, 359; abst. C. A. 1916, **10**, 854.

4. J. Ind. Eng. Chem. 1909, **1**, 4; abst. C. A. 1909, **3**, 693.

5. See Editorial L'Industrie Chimica, **7**, 41; abst. C. A. 1907, **1**, 1460.

ing and profound technical importance, both in the peaceful and in the warlike arts, as has been so remarkably exemplified in the conflict just closed.

The investigations of R. Strutt¹ has proven that under certain conditions nitrogen becomes quite active. "The sp. gr. of N is 0.96717 (air = 1),² one liter weighing 1.2507 gm.³ Nitrogen was liquefied in large quantities by S. Wroblewski⁴ and by K. Olszewski,⁵ the sp. gr. of the liquid at the b. pt. being 0.8042⁶ or 0.8103.⁷ One volume of water dissolves 0.02348 of the gas at 4°, and smaller amounts with rise in temperature.⁸ N is more soluble in ethyl alcohol than in water. While under normal conditions nitrogen is incombustible, a mixture of N and O can be caused to ignite by means of a powerful electric current, and this observation has been the foundation for the commercial transformation of atmospheric nitrogen into nitric acid and water-soluble stable nitrogen compounds synthetically.⁹ The assimilation of nitrogen by plants has been extensively investigated.¹⁰

Stas first determined the atomic weight of nitrogen at 14.04 (O being 16), but later determinations¹¹ have reduced the prob-

1. Proc. Roy. Soc. 1911, **85**, A, 219, 577; 1912, **86**, 262; **87**, 179; 1913, A, **88**, 539; 1915, **91**, 303; Physikal. Zts. 1913, **14**, 215; J. S. C. I. 1915, **34**, 422. E. Tiede, Ber. 1913, **46**, 340. E. Tiede and E. Domeke, Ber. 1913, **46**, 4095; 1914, **47**, 420; J. S. C. I. 1914, **33**, 76, 254.
2. A. Leduc, Compt. rend. 1896, **123**, 805; 1898, **126**, 413.
3. Rayleigh, Proc. Roy. Soc. 1892, **53**, 131; 1894, **55**, 340.
4. Compt. rend. 1883, **97**, 1553; 1884, **98**, 982; 1886, **102**, 1010; Monatsh. 1885, **6**, 204.
5. Compt. rend. 1884, **99**, 133; 1885, **100**, 350.
6. J. Dewar, Proc. Roy. Soc. 1904, **73**, 251.
7. C. Baly and F. Donnan, J. C. S. 1902, **81**, 912; see also W. Ramsay and J. Drugman, J. C. S. 1900, **77**, 1228.
8. L. Winkler, Ber. 1891, **24**, 3605.
9. W. Spottiswoode, Proc. Roy. Soc. 1881, **31**, 173. W. Crookes, Chem. News, 1892, **65**, 302. See also Rayleigh, J. C. S. 1897, **71**, 181. W. Muthmann and H. Hofer, Ber. 1903, **36**, 438.
10. For further details see J. Lawes and J. Gilbert, Phil. Trans. 1890, B, **180**, 1; J. Roy. Agri. Soc. 1891, 657; Proc. Roy. Soc. 1890, **46**, 85. T. Schloesing and E. Laurent, Compt. rend. 1891, **113**, 776. Marshall Ward, Nature, 1893-1894, **49**, 511. For triatomic nitrogen, see M. Trautz, Zts. Elektrochem. 1919, **25**, 297; abstr. J. S. C. I. 1919, **38**, 898-A.
11. J. Hibbs, J. A. C. S. 1896, **18**, 1044. G. Dean, J. C. S. 1900, **77**, 117. A. Scott, J. C. S. 1901, **79**, 147; Proc. Chem. Soc. 1905, **21**, 309. P. Guye, Compt. rend. 1904, **138**, 1213; 1905, **140**, 1241, 1386. P. Guye and S. Bogdan, Compt. rend. 1904, **138**, 1494. A. Jaquerod and S. Bogdan, Compt. rend. 1904, **139**, 49. P. Guye and A. Pintza, Compt. rend. 1905, **141**, 51; 1908, **147**, 925. A. Jaquerod and O. Scheuer, Compt. rend. 1905, **140**, 1384. R. Gray, J. C. S. 1905, **87**, 1601. G. Hinrichs, Compt. rend. 1905, **140**, 1590. T. Richards and G. Forbes, J. A. C. S. 1907, **29**, 808; 1909, **31**, 6. P. Guye and G. Drouguine, J. Chim. Phys. 1910, **8**, 473.

able value to 14.01, while the corrected gasometric density leads to the figures 13.9 and 13.904 as determined by A. Lecluc¹ and by Rayleigh.²

Nitrogen Oxides.³ of which five are possible, and all known,

1. Compt. rend. 1897, **125**, 299. See also D. Berthelot, Compt. rend. 1898, **126**, 1030. M. Vezes, Compt. rend. 1898, **126**, 1714.
2. Proc. Roy. Soc. 1897, **62**, 209; 1904, **73**, 153.
3. For the oxidation of nitrogen at high temperatures, refer to: R. Pawlikowski, E. P. 26728, 1905; D. R. P. 171623. O. Bruenler and G. Kettler, U. S. P. 898033, 1908; abst. J. S. C. I. 1908, **27**, 982; E. P. 5852, 5901, 1906; abst. J. S. C. I. 1906, **25**, 811; D. R. P. 185094; abst. C. A. 1907, **1**, 3073; 205351; F. P. 363617, 363618, 380467; abst. J. S. C. I. 1906, **25**, 199, 846. Chemische Fabrik Griesheim Elektron, E. P. 13954, 1907. O. Bender, U. S. P. 900471; E. P. 8653, 1907; 18203, 1909; F. P. 377442, 405463; abst. J. S. C. I. 1908, **27**, 75; 1910, **29**, 211; D. R. P. 192883, 217079, 217080, 217550, 227490, 277435, 279007, 280966; D. R. P. Appl. B-51927. G. Kettler, E. P. 24264, 1908; F. P. 396161; D. R. P. 209961. Dupre, D. R. Appl. D-19353. K. Soedermann, E. P. 411785, 413117, 416036; abst. J. S. C. I. 1910, **29**, 949, 1377. K. Vietinghoff-Scheel, D. R. P. 222629. F. Haecuser, U. S. P. 1000732; E. P. 12401, 13989, 27826, 1906; 13989, 1907; 20777, 1910; F. P. 409758, 420112; D. R. P. 216518, 218813; abst. Zts. ang. Chem. 1910, **23**, 763; 232569; abst. J. S. C. I. 1911, **30**, 1115; C. A. 1911, **5**, 2709. R. Pictet, E. P. 415594; D. R. P. 226867. Badische Anilin u. Soda Fabrik, E. P. 20406, 1908; F. P. 396375; D. R. P. 219494. W. Phillips and J. Bulteel, E. P. 23976, 1909; 27558, 29893, 1910; 4268, 1911. I. Devilaire, F. P. 423893. Societe l'Air Liquide, F. P. 416557; abst. J. S. C. I. 1910, **29**, 1378. F. Wiegolanski, Norw. P. 20328. J. Alsberge, E. P. 8779, 1889. A. Scherbius, D. R. P. 213709; abst. Wag. Jahr. 1909, **55**, I, 611. A. Scherbius and H. Wach, D. R. P. 221129; abst. Wag. Jahr. 1910, **56**, I, 479. J. Price, E. P. 10755, 1909; 5657, 1910. Saltpetersaure Industrie Ges., D. R. P. 235299; F. P. 420252. Westdeutsche Thomasphosphatwerke, D. R. P. 182297; Aust. P. 24374, 1906; E. P. 25010, 1904; F. P. 348189, 353548; abst. J. S. C. I. 1905, **24**, 441, 1013; Belg. P. 180831, 183940, 199745. G. Pauling, U. S. P. 758774; F. P. 323760, 325244. For data on the electrolytic oxidation of atmospheric nitrogen, consult: E. Herman, D. R. P. 281084, 283535. Atmospheric Products Co., D. R. P. 179288, 1902; abst. Zts. ang. Chem. 1907, **20**, 761. W. Crookes, Electric World, **33**, 319. W. Muthmann and H. Hofer, Ber. 1903, **36**, 438. F. Lepel, Ber. 1897, **30**, 1027; 1903, **36**, 1251; 1904, **37**, 3470. A. Stabenhagen, Ber. 1905, **38**, 2171. A. Grau and F. Russ, Wiener Akad. Ber. Dec. 1906; Zts. Electrochem. 1907, 573. W. Nernst, Zts. anorg. Chem. 1906, **213**, 229. M. Berthelot, Compt. rend. 1906, **142**, 1367. J. Brode, Zts. Electrochem. 1905, **12**, 752. A. Scheuer, Zts. Electrochem. 1905, **12**, 565. M. Bodenstein, Zts. ang. Chem. 1906, **19**, 14. F. Haber (collaborating with Choates, Makowetzky, Holwech, Koenig, and Platou, Zts. ang. Chem. 1910, **31**, 684, 803, 810; Zts. Phys. Chem. 1909, 337. E. Warburg and G. Leithauser, Berl. Akad. Ber. 1907, 229; Pogg. Ann. 1906, (4), **20**, 743; Chem. Centr. 1907, **78**, I, 1173. Fischer and Braehmer, Berl. Ber. 1906, 940, 968. F. Fischer and H. Marx, Ber. 1906, **39**, 2557. Hauser, Zts. Electrochem. 1906, 444; Zts. Verein. Deutsch. Ing. 1912, 1157; Chem. Trade J. 1914, **55**, 46. E. Briner and E. Durand, Compt. rend. 1907, **145**, 248. H. Holwech, Zts. ang. Chem. 1908, **21**, 2131; Zts. Electrochem. 1910, **17**, 369. A. Grau and F. Russ, Zts. ang. Chem. 1908, **21**, 554. F. Howles, J. S. C. I. 1907, **26**, 290. LeBlanc, Zts. Electrochem. 1907, **14**, 297. P. Guye, Mon. Sci. 1907, **66**, 225. M. Bodenstein, Zts. Electrochem. 1910, **17**, 876. F. Forster and J. Blich, Zts. ang. Chem. 1910, **23**, 2017. H. Laveth and C. Rand, Zts. ang. Chem. 1905, **18**, 1906. P. Guye, J. S. C. I. 1906, **25**,

are as follows, according to the increasing nitrogen content:

- (1) Nitrogen Monoxide: nitrous oxide, laughing gas, N_2O .
- (2) Nitrogen Dioxide: nitric oxide, nitrohydroxylaminic anhydride, NO .
- (3) Nitrogen Trioxide: nitrous anhydride, N_2O_3 .
- (4) Nitrogen Tetroxide: nitrogen peroxide, NO_2 .
- (5) Nitrogen Pentoxide: nitric anhydride, N_2O_5 .

The methods for the commercial production of some of these

567. Bull. Soc. Chim. 1909, **5**, 339. A. Neuberger, Zts. ang. Chem. 1905, **18**, 1842. F. Russ, Zts. ang. Chem. 1908, **21**, 555. H. Andriessens, Schweiz. Elektrot. Verein Bull. 1919, **9**, 253; Sci. Abstracts Section B, **22**, 131; abst. C. A. 1919, **13**, 2638. B. Adhikary, Chem. News, 1915, **112**, 163; abst. J. S. C. I. 1915, **34**, 1053. See J. S. C. I. 1911, **30**, 282. O. Baudisch and G. Klinger, Ber. 1912, **45**, 3231; abst. J. S. C. I. 1912, **31**, 1178. I. Bellucci, Gaz. chim. ital. 1914, **44**, II, 384; abst. J. S. C. I. 1914, **33**, 384. F. Benna, E. P. 125453, 1916; abst. C. A. 1919, **13**, 2259. M. Bodenstein, Zts. Elektrochem. 1918, **24**, 183; abst. J. S. C. I. 1918, **37**, 504-A; C. A. 1918, **12**, 2291; J. S. C. I. 1918, **37**, 504-A. E. Briner, Helv. Chim. Acta, 1919, **2**, 162; abst. J. C. S. 1919, **116**, ii 190; J. S. C. I. 1919, **38**, 284-A. E. Briner and A. Baerfuss, J. Chim. Phys. 1919, **17**, 71; abst. J. C. S. 1919, **116**, ii, 338; J. S. C. I. 1919, **38**, 572-A; Helv. Chim. Acta, 1919, **2**, 95; abst. J. C. S. 1919, **116**, ii, 148; J. S. C. I. 1919, **38**, 219-A. E. Briner and E. Fridori, Helvetica Chim. Acta, 1918, **1**, 181; abst. C. A. 1919, **13**, 100; J. Chim. Phys. 1918, **16**, 279; J. S. C. I. 1918, **37**, 504-A. E. Briner and P. Naville, J. Chim. Phys. 1919, **17**, 329; abst. C. A. 1919, **13**, 2487, 3090; Helv. Chim. Acta, 1919, **2**, 348; abst. J. S. C. I. 1919, **38**, 814-A; J. C. S. 1919, **116**, ii, 464. F. Carpenter, J. S. C. I. 1886, **5**, 287. J. Coates and A. Finney, J. C. S. 1914, **105**, 2444; abst. J. S. C. I. 1914, **33**, 1206. Comte, Phys. Zts. 1913, **14**, 74. R. Drawe, U. S. P. 1283112, 1918; abst. J. S. C. I. 1919, **38**, 73-A. F. du Pont, U. S. P. 1311594, 1919; abst. C. A. 1919, **13**, 2488; J. S. C. I. 1919, **38**, 681-A. R. Esnault-Pelterie, E. P. 100275; Chem. News, 1913, **108**, 178; abst. J. S. C. I. 1913, **32**, 975. F. Fischer and E. Hene, Ber. 1912, **45**, 3652; 1913, **46**, 603; abst. J. S. C. I. 1913, **32**, 82, 288. F. Foerster and M. Koch, Zts. ang. Chem. 1908, **21**, 2161, 2209; abst. J. S. C. I. 1909, **27**, 1110. A. Grieppe, Amer. Gas J. 1918, **109**, 487, 492; abst. C. A. 1919, **13**, 637. P. Guye and F. Schneider, Helv. Chim. Acta, 1918, **1**, 33; abst. J. S. C. I. 1918, **37**, 412-A; C. A. 1918, **12**, 1865. F. Haber and A. Koenig, Zts. Elektrochem. 1907, **13**, 725. E. Haslup, U. S. P. 1310480, 1919; abst. C. A. 1919, **13**, 2427. O. Jensen, U. S. P. 1291909, 1919; abst. J. S. C. I. 1919, **38**, 285-A; C. A. 1919, **13**, 998. P. Jolibois and A. Sanfourche, Compt. rend. 1919, **168**, 235; abst. C. A. 1919, **13**, 1055; J. S. C. I. 1919, **38**, 132-A. G. Klinger, Ber. 1913, **46**, 1744; abst. J. S. C. I. 1913, **32**, 697. A. Koenig, Ber. 1913, **46**, 132; abst. J. S. C. I. 1913, **32**, 194. J. LaCour, U. S. P. 1296194; abst. C. A. 1919, **13**, 1428. W. Landis, U. S. P. 1292814, 1919; abst. J. S. C. I. 1919, **38**, 285-A. G. Lewis and E. Adams, J. A. C. S. 1915, **37**, 2308; abst. J. S. C. I. 1915, **34**, 1141. W. Loeb, Zts. Elektrochem. 1908, **14**, 556; abst. J. S. C. I. 1908, **27**, 945. W. Manchot, Ann. 1910, **375**, 308; abst. J. S. C. I. 1910, **29**, 1202; Ber. 1914, **47**, 1601; abst. J. S. C. I. 1914, **33**, 642. W. Manchot and F. Huttner, Ann. 1910, **372**, 153; abst. J. S. C. I. 1910, **29**, 563. F. Russ, Zts. ang. Chem. 1908, **21**, 486; abst. J. S. C. I. 1908, **27**, 333. E. Maxted and G. Ridsdale, E. P. 10781, 1915; 126083, 127645, 1917; abst. J. S. C. I. 1919, **38**, 252-A; 344-A; C. A. 1919, **13**, 1625, 2427. W. Moldenhauer and O. Wehrheim, Zts. ang. Chem. 1914, **27**, 334; abst. J. S. C. I. 1914, **33**, 748. C. Montgomery and E. Royston, E. P. 131609, 1916; abst. J. S.

oxides are of great importance, forming, as they do, stepping stones in the synthesis of nitric acid. F. Foerster and J. Blich have shown¹ that the oxidation of NO by free O to NO₂ between 0° and 100° occurs more rapidly at lower than at higher temperatures. G. Lunge and E. Berl have pointed out² that the proportion of nitrous and nitric acids in the atmospheric oxidation of N₂ is 1:1. 1919, **38**, 764-A. L. Moser, Zts. anal. Chem. 1911, **50**, 401; abst. J. S. C. I. 1911, **30**, 802. E. Mueller, Zts. anorg. Chem. 1912, **76**, 324; abst. J. S. C. I. 1912, **31**, 685. W. Muthmann and H. Hafer, Ber. 1903, **36**, 438; abst. J. S. C. I. 1903, **22**, 303. Norsk Hydro-Elektrisk Kvael, D. R. P. 310859, 1919; abst. Chem. Zentr. 1919, **90**, II, 339. T. Panzer, Zts. Physiol. Chem. 1915, **93**, 378; abst. J. S. C. I. 1915, **34**, 514. A. Pinkus, Helv. Chim. Acta, 1918, **1**, 141; abst. J. S. C. I. 1918, **37**, 504-A. E. Rossi, Gaz. Chim. ital. 1905, **35**, 89; abst. J. S. C. I. 1905, **24**, 672; Chem. Centr. 1905, **76**, I, 1525. A. Sanfourche, Compt. rend. 1919, **168**, 235, 307, 401; abst. J. S. C. I. 1919, **38**, 132-A, 172-A, 219-A; C. A. 1919, **13**, 1055. A. Sapozhnikow, A. Goudima and V. Koutovski, J. Russ. Phys. Chem. Soc. 1913, **45**, 1076; abst. J. S. C. I. 1913, **32**, 975. V. Thomas, Bull. Soc. Chim. 1895, **13**, 385. E. Tiede, Ber. 1913, **46**, 340; abst. J. S. C. I. 1913, **32**, 232. O. Tower, Zts. anorg. Chem. 1906, **50**, 382; abst. J. S. C. I. 1906, **25**, 1043. E. Wuest, E. P. 104734; abst. J. S. C. I. 1917, **36**, 548. W. Cramp and B. Hoyle, J. S. C. I. 1909, **28**, 95. V. Ehrlich and F. Russ, Sitzungsberichte der Kais. Akad. d. Wiss. in Wien, 1911, **120**, July; Monatsh. 1911, 917. R. Pearson and H. Parkes, E. P. 130693, 1918; abst. C. A. 1920, **14**, 103. F. Gerhardt, D. R. P. 303255, abst. J. S. C. I. 1919, **38**, 891-A. Harburger Chemische Werke Schön & Co. and W. Daitz, D. R. P. 298911; abst. J. S. C. I. 1920, **39**, 21-A. Matignon, Chem. Trade J. 1914, **55**, 69. Kochler and Marueyrol, Bull. Soc. Chim. 1913, **13**, 69; abst. J. S. C. I. 1913, **32**, 140. B. Bunet and A. Badin, E. P. 16224, 16225, 1909; abst. J. S. C. I. 1910, **29**, 98, 277; U. S. P. 1035684; abst. C. A. 1912, **6**, 3232; Mon. Sci. 1913, **79**, 12; F. P. 402012, 406115; abst. J. S. C. I. 1909, **28**, 1198; 1910, **29**, 98, 1212, 1377; 1912, **31**, 817; Mon. Sci. 1910, **73**, 167; 1911, **75**, 572; 1910, **73**, 173; 1911, **75**, 571, 572. D. Timar, F. P. 412227; Aust. P. 48537; abst. J. S. C. I. 1910, **29**, 1010. F. duPont, U. S. P. 948372, 950703; abst. Mon. Sci. 1910, **73**, 119, 133; Chem. Ztg. Rep. 1910, **34**, 126, 179; J. S. C. I. 1910, **29**, 353, 423. A. Grau and F. Russ, Sitzungsber. d. Wien Akad. 1906, **115** (ii a); 1908, **117** (ii a), 321; Elektrochem. Zts. 1907, **13**, 345, 573; J. C. S. 1906, **92**, ii, 601; 1908, ii, 753. E. Rossi, Gaz. chim. ital. 1905, **35**, I, 89; J. C. S. 1905, **88**, ii, 386; Zts. Elektrochem. 1905, **2**, 504. A. Gorjainoff, Belg. P. 191060, 193262, 1906. E. Geisenberger, Belg. P. 216728, 1909. F. Hacussier, Belg. P. 200795, 1907; 221089, 1909; 228566, 1910. F. Ilavati, Belg. P. 252772, 1913. Meister, Lucius & Bruening, Belg. P. 234947, 1911; 253381, 262810, 1913; Swiss P. 55537, 1911; 65129, 1913. K. Soederman, Swiss P. 52268, 1910. Societe Anonyme L'Air Liquide, Belg. P. 227869, 1910. R. Pictet, Belg. P. 156203, 1901; 224987, 1910; E. P. 19254, 1900; J. S. C. I. 1901, **20**, 1194; see also Engineering, 1901, 368; J. S. C. I. 1901, **20**, 985. W. Phillips and J. Bulteel, Swiss P. 57535, 1911. L. Roth, Belg. P. 208231, 1908. C. Tellier, Belg. P. 190772, 1906. F. Timm, Aust. P. 11677, 1903; abst. Chem. Zts. 1903, **2**, 543. For the use of nitrous oxide as gaseous fuel in explosion motors, see Morun, F. P. 317543, 1902; abst. J. S. C. I. 1902, **21**, 1447.

1. Zts. ang. Chem. 1910, **23**, 2018. Atmospheric Products Co., U. S. P. 709867; abst. Chem. Ztg. 1902, **26**, 1018; 709868; E. P. 8230, 1901; 14781, 1902; abst. J. S. C. I. 1901, **20**, 726; 1902, **21**, 1282; Swiss P. 24229.

2. Chem. Ztg. 1904, **28**, 1243. R. Samuel, E. P. 1670, 1915; abst. J. S. C. I. 1916, **35**, 315.

tion of NO are not influenced by the dilution of the oxygen, but by the quantity of water present and the intensity and intimacy of agitation. In another method,¹ NO is converted into HNO₃, preferably by alternate instead of simultaneous treatment with oxygen and water. They² allege that when the higher nitrogen oxides are absorbed by sulfuric acid, N₂O₅ is absorbed without the formation of HNO₃. In another patented process,³ a current of air containing nitrogen oxides is caused to meet an opposing current of alkaline solution in a series of towers, whereby alkaline nitrite and nitrate are formed, the latter being readily separated from the former by crystallization. Verge⁴ claims an improved

1. P. Naëlle, A. and C. Guye, F. P. 253192, 361827, 385569; abst. J. S. C. I. 1907, **26**, 23, 209; 1908, **27**, 627; Chem. Ztg. Rep. 1907, **31**, 72; Mon. Sci. 1909, **71**, 106. D. R. P. 88320, 1895; abst. Chem. Ztg. 1896, **20**, 825; Wag. Jahr. 1896, **42**, 334; Zts. ang. Chem. 1896, **9**, 623. D. R. P. 187585; abst. Chem. Zentr. 1907, **78**, II, 1278; Chem. Ztg. Rep. 1907, **31**, 479; Jahr. Chem. 1905-1908, II, 3619; Wag. Jahr. 1907, **53**, I, 403; Zts. ang. Chem. 1908, **21**, 557. E. P. 6155, 6366, 1907; abst. Zts. Elektrochem. 1902-1903, **9**, 623.

2. F. P. 350120, 385605; abst. J. S. C. I. 1905, **24**, 1178; 1910, **29**, 117; Mon. Sci. 1911, **75**, 572, 573. D. R. P. 225153; abst. Chem. Zentr. 1910; **81**, II, 1103; Chem. Ztg. Rep. 1910, **34**, 198; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 487; Zts. ang. Chem. 1910, **23**, 2189. E. P. 21338, 1906; abst. J. S. C. I. 1907, **26**, 1015. F. Raschig, Chem. Ztg. 1907, **31**, 359; J. S. C. I. 1907, **26**, 686; Zts. ang. Chem. 1907, **20**, 702. W. Phillips, U. S. P. 1035732; abst. J. S. C. I. 1912, **31**, 817, C. A. 1912, **6**, 3315; Mon. Sci. 1913, **79**, I. K. Kaiser, Belg. P. 182087, 1905; 228365, 1910; 240921, 1911; Swiss P. 51446, 54320, 1910; 59410, 1911. G. Kettler, Swiss P. 40882, 1907; 43779, 1908; Belg. P. 211919, 1908. D. Timar, Belg. P. 222809, 1910. C. Torley and O. Matter, Belg. P. 256752, 1913. In this connection refer to C. Guye, U. S. P. 1109330; abst. C. A. 1914, **8**, 3398; E. P. 804, 1912; abst. C. A. 1913, **7**, 2163; J. S. C. I. 1912, **31**, 825; F. P. 438783; abst. J. S. C. I. 1912, **31**, 649. C. Guye and A. Brom, Arch. Sci. Phys. et Nat. 1908, **25**, 453; Compt. rend. 1908, **146**, 1090; 1908, **147**, 49. C. Guye and L. Sebrinkoff, Arch. Sci. Phys. Nat. 1907, **24**, 549; abst. C. A. 1913, **7**, 1788; Mon. Sci. 1913, **79**, 146; Chem. Ztg. Rep. 1913, **37**, 447. P. Guye, U. S. P. 1057052, F. P. 441002, abst. J. S. C. I. 1911, **30**, 541. U. S. P. 1035581, F. P. 420524, abst. J. S. C. I. 1911, **30**, 372; 1912, **31**, 825; C. A. 1912, **6**, 3211; Mon. Sci. 1913, **79**, 12. F. P. 389864; abst. J. S. C. I. 1908, **27**, 1032; abst. Mon. Sci. 1909, **71**, 112. F. P. 404630, abst. J. S. C. I. 1911, **30**, 211; J. S. C. I. 1906, **25**, 627; Met. Chem. Eng. 1906, **4**, 136; Mon. Sci. 1907, **21**, 225; Mon. Sci. 1910, **73**, 170. Nitrogen Ltd., Belg. P. 237542, 1911.

3. The Saltpetresäure Industrie-Ges. Gelsenkirchen and Pauling, E. P. 9881, 1910; abst. J. S. C. I. 1910, **29**, 1157.

4. F. P. 409194; abst. Mon. Sci. 1911, **75**, 146, 571, 572. See F. P. 339730, 370977, 377199, 380121, 385569, 388281, 388308, 392670, 398424, 405463, 411785, 412227, 412788, 413117, 415594, 416224, 420112, addn. 12327 to 413117, 422751, 428657, 430060, 430112, 439113, 432810, and addn. 13519, 437397, addn. 15151, 15619, 15923 to 436789. O. Dahl, F. P. 391822, 399832; abst. J. S. C. I. 1908, **27**, 1152; abst. Mon. Sci. 1911, **75**, 571. A. MacDougall, E. P. 4643, 1899; abst. J. S. C. I. 1900, **19**, 649. Swiss P. 20092; abst. J. S. C. I. 1900, **19**, 349; Zts. ang. Chem. 1904, **17**, 1717. See A. MacDougall and W. Howles, Man. Lit. and Phil. Soc. Mem. 1900, **44**, 1.

yield of nitrogen in the synthetic process, by cooling the nitrogen gases immediately upon their liberation by means of liquid air. In this manner the solid oxides may be filtered off and treated with air and water to obtain nitric acid of high concentration. The absorption of nitrogen gases by dilute lime and kept in motion by means of rapidly revolving drums, forms the essence of another¹ invention. O. Bender² produces oxides of nitrogen by burning fuel gas in the form of small pointed flames, supporting combustion by a mixture of oxygen and air in such proportion that the resulting gases are high in NO and NO₂. The Badische Anilin und Soda Fabrik³ is similar. Atmospherically diluted oxides of nitrogen may also be absorbed in a weak basic oxide, as the oxides of copper, lead or zinc,⁴ which are afterwards heated to high temperatures to liberate the nitrogen oxides.

Bender's patents for obtaining nitrogen-oxygen compounds,⁵ burn fuel in air under high pressure with water atomized, alum-

1. Norske Aktieselskab for Elektrotesmisk Industri and B. Halvorsen, F. P. 380190; abst. J. S. C. I. 1907, **26**, 1280; Chem. Ztg. Rep. 1907, **31**, 633. H. Schefflein, F. P. 431515; abst. J. S. C. I. 1913, **32**, 601. For the J. Island device for producing nitrogen oxides, see L. S. P. 1082529; abst. C. A. 1914, **8**, 632; Mon. Sci. 1914, **81**, 65. 1179927, abst. J. S. C. I. 1916, **35**, 633. E. P. 113663, 1912; abst. C. A. 1913, **7**, 3576; J. S. C. I. 1913, **32**, 909. F. P. 460557; abst. J. S. C. I. 1913, **32**, 909; 1916, **35**, 633; C. A. 1914, **8**, 3156.
2. C. A. 1911, **5**, 1665, 1667. Swiss P. 49601, 1909. Belg. P. 199245, 218026. U. S. P. 1011014, abst. C. A. 1912, **6**, 415; J. S. C. I. 1910, **29**, 152. D. R. P. 249447, 1912; abst. J. S. C. I. 1915, **34**, 27; Wag. Jahr. 1912, **58**, I, 382; Chem. Zentr. 1912, **83**, II, 464; Chem. Ztg. Rep. 1912, **36**, 481; Zts. ang. Chem. 1912, **25**, 1929; C. A. 1912, **6**, 3170.
3. E. P. 30502, 1909; 30503, 1909; abst. C. A. 1911, **5**, 2921; J. S. C. I. 1910, **29**, 1455; 1911, **30**, 87. See also D. R. P. 229780, C. A. 1911, **5**, 2536. D. R. P. 233982, 1909; abst. C. A. 1911, **5**, 2921; Chem. Zentr. 1911, **81**, I, 1466; Chem. Ztg. Rep. 1911, **35**, 262; Wag. Jahr. 1911, **57**, I, 467; Zts. Schiess. Spreng. 1911, **6**, 232. D. R. P. 237562, 1910; add. to D. R. P. 233982, abst. C. A. 1912, **6**, 1508; Chem. Zentr. 1911, **82**, II, 812; Chem. Ztg. Rep. 1911, **35**, 438; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 1782; Zts. Schiess. Spreng. 1911, **6**, 354.
4. Allgemeine Elektrizitäts Ges., E. P. 8426, 1908; abst. J. S. C. I. 1909, **28**, 937; C. A. 1910, **4**, 91; E. P. 9233, 1908; abst. C. A. 1909, **3**, 825; J. S. C. I. 1908, **27**, 940. See also D. R. P. 199561; abst. J. S. C. I. 1908, **27**, 856. See also G. Brisset and M. Muguet, F. P. 375349; abst. J. S. C. I. 1908, **27**, 930; Mon. Sci. 1911, **75**, 571, 572.
5. D. R. P. 277435, 279007, 280966; abst. J. S. C. I. 1915, **34**, 228; Chem. Zentr. 1914, **85**, II, 673, 1079; 1915, **86**, I, 175; Chem. Ztg. Rep. 1914, **38**, 479, 527; 1915, **39**, 3; Zts. ang. Chem. 1914, **27**, 564, 622; 1915, **28**, 82; Wag. Jahr. 1914, **60**, I, 353, 446; Mon. Sci. 1917, **84**, 73. W. Lachmann, D. R. P. 289844; abst. J. S. C. I. 1916, **35**, 538; Chem. Zentr. 1916, **87**, I, 349; Chem. Ztg. Rep. 1916, **40**, 101; Zts. ang. Chem. 1916, **29**, 137. O. Bruenler, Belg. P. 190204, 190205, 1906. P. Bunet and A. Badin, Belg. P. 217328, 1909; Swiss P. 49600, 1909.

inum oxide¹ being used as a nitrogen carrier, as also has bismuth oxide² and tellurium or a tellurium compound.³ F. Bayer & Co.⁴ separate nitrogen oxides from admixture with other gases by means of wood charcoal as an absorbent, the gases being sub-

1. U. S. P. 1172863, abst. J. S. C. I. 1916, **35**, 468. E. P. 474107. E. P. 18203, 1909; abst. C. A. 1910, **4**, 2555; abst. Mon. Sci. 1916, **83**, 82; J. S. C. I. 1910, **29**, 211. D. R. P. 217079, 1908; abst. C. A. 1910, **4**, 1092; Mon. Sci. 1913, **79**, 157; Chem. Zentr. 1910, **81**, I, 307; Chem. Ztg. Rep. 1910, **34**, 63; Jahr. Chem. 1909, **62**, I, 530; Wag. Jahr. 1909, **55**, I, 413; Zts. ang. Chem. 1910, **23**, 380; Zts. Schiess. Spreng. 1910, **5**, 53; D. R. P. 217550, 1908; abst. C. A. 1910, **4**, 1531; Mon. Sci. 1913, **79**, 157; Chem. Zentr. 1910, **81**, I, 585; Chem. Ztg. Rep. 1910, **34**, 84; Jahr. Chem. 1910, **63**, I, 584; Zts. ang. Chem. 1910, **23**, 380; Zts. Schiess. Spreng. 1910, **5**, 53; D. R. P. 277490, 1909; abst. C. A. 1911, **5**, 1667; Chem. Ztg. 1914, **38**, 531. Soc. Anon. d'Études Electrochimiques. E. P. 13952, 1904. E. P. 350120; abst. Mon. Sci. 1911, **75**, 572, 573; J. S. C. I. 1905, **24**, 550. D. R. P. 187585, 1903; abst. J. S. C. I. 1905, **24**, 550; Zts. ang. Chem. 1908, **21**, 557; Chem. Zentr. 1907, **78**, II, 1278; Chem. Ztg. Rep. 1907, **31**, 479; Jahr. Chem. 1905-1908, I, 1768; Wag. Jahr. 1907, **53**, I, 403; Zts. ang. Chem. 1908, **21**, 557.

2. Badische Anilin u. Soda Fabr., E. P. 13848, 1914; abst. J. S. C. I. 1915, **34**, 799. E. P. 7651, 1915; abst. J. S. C. I. 1916, **35**, 1015.

3. Badische Anilin u. Soda Fabr., E. P. 20406, 1908; abst. J. S. C. I. 1909, **28**, 937. E. P. 30503, 1909; abst. J. S. C. I. 1911, **30**, 87. E. P. 13297, 1915; abst. J. S. C. I. 1916, **35**, 1108. E. P. 13298, 1915; abst. J. S. C. I. 1916, **35**, 1015. D. R. P. 188188, abst. C. A. 1908, **2**, 576; Chem. Zentr. 1907, **78**, II, 1282; Chem. Ztg. Rep. 1907, **31**, 492; Chem. Zts. 1907, **6**, No. 200; Jahr. Chem. 1905-1908, I, 1779; Wag. Jahr. 1907, **53**, I, 413. D. R. P. 219494, 1908; abst. C. A. 1910, **4**, 2032; Chem. Zentr. 1910, **81**, I, 971; Chem. Ztg. Rep. 1910, **34**, 142; Chem. Zts. 1910, **9**, No. 1924; Jahr. Chem. 1910, **63**, I, 584; Wag. Jahr. 1910, **56**, I, 471; Zts. ang. Chem. 1910, **23**, 1049; Zts. Schiess. Spreng. 1910, **5**, 175. D. R. P. 233967, 1909; abst. C. A. 1911, **4**, 2921; Chem. Zentr. 1911, **82**, I, 1466; Chem. Ztg. Rep. 1911, **35**, 234; Wag. Jahr. 1911, **57**, I, 467; Zts. ang. Chem. 1911, **24**, 1003; Zts. Schiess. Spreng. 1911, **6**, 232. J. Hayden, U. S. P. 1066272; abst. J. S. C. I. 1913, **32**, 977; C. A. 1913, **7**, 2724; Mon. Sci. 1914, **81**, 22. W. Radley, E. P. 1450, 1856. A. Schweitzer and F. Hauff, E. P. 3410, 1912; abst. C. A. 1913, **7**, 2517. U. S. P. 1037061, abst. J. S. C. I. 1912, **31**, 876; C. A. 1912, **6**, 3232; Mon. Sci. 1913, **79**, 5. E. P. 439872; abst. J. S. C. I. 1912, **31**, 721. W. Siebert, U. S. P. 1033126; abst. J. S. C. I. 1912, **31**, 782; C. A. 1912, **6**, 2580.

4. E. P. 423760, 1910; abst. C. A. 1912, **6**, 1969; Mon. Sci. 1913, **79**, 117; Chem. Ztg. Rep. 1911, **35**, 306. See also Atmospheric Products Co., D. R. P. 179288, abst. C. A. 1907, **1**, 1462; Mon. Sci. 1909, **71**, 74; Chem. Zentr. 1907, **78**, I, 430; Chem. Ztg. Rep. 1907, **30**, 11; Chem. Zts. 1907, **6**, 258; Jahr. Chem. 1905-1908, I, 1764; Wag. Jahr. 1906, **52**, I, 456; Zts. ang. Chem. 1907, **20**, 761. Baudisch, Zts. ang. Chem. 1913, **27**, 612. U. S. P. 991357; abst. C. A. 1911, **5**, 2312; Mon. Sci. 1912, **77**, 17. E. P. 22322, 1910; abst. C. A. 1911, **5**, 2920; J. S. C. I. 1911, **30**, 84. E. Aumont, D. R. P. 233982, addn. to D. R. P. 233967; abst. C. A. 1911, **5**, 2921; Chem. Zentr. 1911, **81**, I, 1466; Chem. Ztg. Rep. 1911, **35**, 262; Wag. Jahr. 1911, **57**, I, 467; Zts. Schiess. Spreng. 1911, **6**, 232. D. R. P. 260758, 1911; abst. C. A. 1913, **7**, 3206; Chem. Zentr. 1913, **84**, I, 195; Chem. Ztg. Rep. 1913, **37**, 372; Wag. Jahr. 1913, **59**, I, 538; Zts. ang. Chem. 1913, **26**, 412. J. Roberts, U. S. P. 902607; abst. J. S. C. I. 1908, **27**, 1167; Mon. Sci. 1909, **71**, 126. E. Marquardt and H. Viertel, U. S. P. 804021, 1905; Mon. Sci. 1906, **65**, 65. R. Mahnsen, D. R. P. 63036; abst. Wag. Jahr. 1892, **38**, 1123; Zts. ang. Chem. 1892, **5**, 496. E. Mack, E. P. 477476; J. S. C. I. 1916, **35**, 608.

sequently recovered from the charcoal by treatment with steam, hot air or an indifferent gas. In the L. Bergfeld scheme,¹ higher nitrogen oxides are produced from lower ones by a continuous cycle of operations. Bergius² produces concentrated nitric acid from mixtures of gaseous nitrogen peroxide with gases containing oxygen, by causing the reaction to take place at higher temperatures and at an elevated temperature to minimize re-decomposition.

O. Jensen³ absorbs diluted nitrous gases in 90% sulfuric acid, after which the solution is heated with the employment of dephlegmators, whereby concentrated nitrogen oxides are evolved. In the process as described by P. Guye,⁴ gases containing N_2O_3 and NO_2 are recovered by introducing them into a heat-inter-chamber after compression, where they are cooled by expansion to precipitate the nitrous vapors, and the nitric peroxide recovered by means of solvents.⁵

H. Knottenbelt⁶ prepares NO by adding sulfuric acid to a mixture of sodium nitrate and ferrous sulfate; while the Canada Explosives Co.⁷ convert lower into higher nitrogen oxides in a

1. E. P. 21211, 1913; abst. J. S. C. I. 1914, **33**, 831. E. Spitzer, E. P. 22201, 1907; abst. J. S. C. I. 1908, **27**, 27. F. P. 383078, 383136; abst. J. S. C. I. 1908, **27**, 281; Mon. Sci. 1909, **71**, 103; 1911, **75**, 572; Chem. Ztg. 1908, **32**, 164, 165, 452.

2. D. R. P. Anm. B. 53617. Dynamit A.-G. vorm. Nobel & Co., E. P. 3342, 1912; abst. C. A. 1913, **7**, 2516; J. S. C. I. 1913, **32**, 296. D. R. P. 228849, 242210; abst. C. A. 1912, **6**, 2039; Chem. Zentr. 1911, **57**, I, 49; 1912, **83**, I, 295; Chem. Ztg. Rep. 1911, **35**, 3; 1912, **36**, 59; Wag. Jahr. 1910, **56**, I, 464; 1912, **58**, I, 497; Zts. ang. Chem. 1911, **24**, 87; 1912, **25**, 327. F. P. 433836; abst. J. S. C. I. 1911, **30**, 86; 1912, **31**, 1211.

3. Can. P. 170816, 1916; abst. C. A. 1918, **12**, 747; Norw. P. 27317, 1916; abst. C. A. 1917, **11**, 278. F. duPont, U. S. P. 943661, 1147150; abst. J. S. C. I. 1915, **34**, 961; Mon. Sci. 1910, **73**, 84. F. Russ and L. Ehrlich, E. P. 10992, 1912; abst. C. A. 1913, **7**, 3576; J. S. C. I. 1913, **32**, 657. F. Russ, Zts. ang. Chem. 1912, **25**, 586; abst. J. S. C. I. 1912, **31**, 383.

4. U. S. P. 1057052; abst. C. A. 1913, **7**, 1788; Mon. Sci. 1913, **79**, 146; Chem. Ztg. Rep. 1913, **37**, 447. F. P. 404630, 1908; abst. C. A. 1911, **5**, 1664; Mon. Sci. 1910, **73**, 170. Swiss P. 42733, 1908.

5. Norske Aktieselskab for Elektrokemist and B. Halvorsen, U. S. P. 892516; abst. Mon. Sci. 1909, **71**, 113; Chem. Ztg. Rep. 1908, **32**, 423; F. P. 363157; abst. Mon. Sci. 1907, **67**, 92. U. S. P. 910530; abst. C. A. 1909, **3**, 1065; Mon. Sci. 1909, **71**, 139. U. S. P. 948726; abst. Mon. Sci. 1910, **73**, 84. F. P. 380190; abst. Chem. Ztg. Rep. 1907, **31**, 633. Swiss P. 44092, 1908. W. Ramsay, E. P. 16067, 16068, 26981, 1907; abst. J. S. C. I. 1908, **27**, 856; 1909, **28**, 599; C. A. 1909, **3**, 2493. Compare W. Ramsay and J. Cundall, J. C. S. 1885, **47**, 187, 672; 1890, **57**, 590. H. Rankin, F. P. 479492; abst. J. S. C. I. 1916, **35**, 1108.

6. E. P. 18001, 1909; abst. J. S. C. I. 1910, **29**, 999.

7. Can. P. 142472, 1912; abst. C. A. 1913, **7**, 224. T. Young and J. Pettigrew, E. P. 14735, 1884; abst. J. S. C. I. 1885, **4**, 364.

similar manner to that of F. duPont¹ by subjecting air in a non-conducting container surrounded by a cooling jacket, to the action of a rotating arc extending longitudinally in the container and against its inner surface. B. Dut and S. Sen have shown² that when NO is passed into a suspension of lead peroxide in water, a mixture of lead nitrite and nitrate is formed, a portion of the nitrite with an excess of lead peroxide forming the nitrate. The Elektrochemische Werke³ use zinc, copper, manganese or lead for this same purpose. A. Lynn⁴ passed a mixture of O and N over fireclay, heated highly by means of gaseous fuel, with or without steam, the processes of Soc. Anon Le Nitrogene,⁵ and the Saltpeter saure Ind. Ges. being somewhat similar.⁶

W. Phillips has described⁷ a method of obtaining oxides of nitrogen whereby a hydrocarbon flame is spread over a plate and a mixture of N and O allowed to travel through this flame at a speed greater than the speed of the hot gases in the flame. G. Ogston⁸ converts waste nitrogen oxides into nitric acid by the simultaneous action of compressed air and water vapor. The processes of F. Haussner⁹ comprise the manufacture of NO from

1. U. S. P. 948372; abst. C. A. 1910, **4**, 1089; Mon. Sci. 1910, **73**, 119; Chem. Ztg. Rep. 1910, **34**, 126.

2. J. Proc. Asiatic Soc. Bengal, 1914, NS **10**, 287; abst. J. S. C. I. 1917, **112**, ii, 85; J. S. C. I. 1917, **36**, 338. E. Troye, U. S. P. 1156192; abst. J. S. C. I. 1915, **34**, 1152. E. Troye and E. Edwin, U. S. P. 1122555. E. P. 474104; abst. J. S. C. I. 1915, **34**, 132.

3. E. P. 388305, 1908; abst. J. S. C. I. 1908, **27**, 939; Mon. Sci. 1909, **71**, 110; Chem. Ztg. Rep. 1908, **32**, 452.

4. E. P. 3194, 1913; abst. J. S. C. I. 1914, **33**, 352; C. A. 1914, **8**, 2926; Chem. Ztg. Rep. 1914, **38**, 230. I. Moscicki, Belg. P. 201874, 1907; 211302, 1908; Swiss P. 45638, 1908.

5. E. P. 21721, 28933, 1910; 1143, 1911; abst. Chem. Ztg. Rep. 1912, **36**, 371. E. P. 404720, 1909. Swiss P. 44368, 44683, 1908; Swiss P. 47432, 1909; 50366, 1910; 50705.

6. E. P. 22319, 1910; abst. J. S. C. I. 1911, **30**, 685. E. P. 420252, 1910; abst. C. A. 1912, **6**, 1967; Mon. Sci. 1911, **75**, 572; 1913, **79**, 88; Chem. Ztg. Rep. 1911, **35**, 303. D. R. P. 237684; abst. C. A. 1912, **6**, 1508; Chem. Zentr. 1911, **82**, II, 812; Chem. Ztg. Rep. 1911, **35**, 464; Wag. Jahr. 1911, **57**, I, 472; Zts. ang. Chem. 1911, **24**, 1882; Zts. Schiess. Spreng. 1911, **6**, 411. Belg. P. 191508, 194275, 194277, 1906; 211711, 1908; 219580, 1909; 228740, 1910; 234494, 236060, 236061, 1911. Swiss P. 53772, 1910; 57532, 1911.

7. E. P. 27558, 1910; abst. C. A. 1912, **6**, 1506; J. S. C. I. 1911, **30**, 1211. Can. P. 137511, 1914; abst. C. A. 1912, **6**, 797.

8. E. P. 3017, 1862. G. Mordau, Trans. Amer. Electrochem. Soc. 1908, **14**, 113.

9. E. P. 13898, 1907; 27826, 1909; abst. C. A. 1911, **5**, 2706; J. S. C. I. 1910, **29**, 1250. 20777, 1910; abst. C. A. 1912, **6**, 1346; J. S. C. I. 1911, **30**, 1117, 7419, 1914; abst. C. A. 1912, **6**, 1346; J. S. C. I. 1915, **34**, 800. D. R. P. 216318, 1907; abst. C. A. 1910, **4**, 818; Mon. Sci. 1913, **79**, 157;

a compressed explosive mixture of N and O and a suitable combustible in the form of a vapor or gas, the mixture being exploded in a bomb. A. Knowles¹ purifies electrolytically generated gases by means of catalytically acting substances.

- The methods of F. Sparre,² L. Summers,³ A. Sinding-Larsen,⁴ Siemens & Halske Akt. Ges.,⁵ E. Shackleton,⁶ M. Rohmer,⁷ A. Reynoso,⁸ E. Prytz⁹ and A. Pauling¹⁰ are similar in principle to those already described. C. Krauss and P. Staehlin¹¹ prepare
- Chem. Zentr. 1910, **81**, 1, 129; Chem. Ztg. Rep. 1910, **34**, 19; Chem. Zts. 1910, **9**, No. 1564; Jahr. Chem. 1909, **62**, 1, 530; Wag. Jahr. 1909, **55**, 1, 415; Zts. ang. Chem. 1910, **23**, 228; Zts. Schiess. Spreng. 1910, **5**, 61; J. S. C. I. 1910, **29**, 25. Can. P. 131650, 1911; abst. C. A. 1911, **5**, 1980. F. P. 409513, 409758, 420112, 469649; abst. J. S. C. I. 1910, **29**, 696; 1911, **30**, 360; 1915, **34**, 80. Zts. ang. Chem. 1906, **19**, 341; Zts. Ver. Deut. Ing. 1906, **50**, 298; 1912, **56**, 1157; Chem. Ztg. Rep. 1910, **34**, 259; abst. Mon. Sci. 1913, **79**, 88. E. P. 7419, 1914; abst. J. S. C. I. 1915, **34**, 800; C. A. 1912, **6**, 1346. See also Hempel, Ber. 1890, **23**, 1455. K. Finkh, Zts. anorg. Chem. 1905, **45**, 116.
1. D. R. P. 261306; abst. C. A. 1913, **7**, 3577; Chem. Ztg. Rep. 1913, **37**, 448; Wag. Jahr. 1913, **59**, 1, 510; Zts. ang. Chem. 1913, **26**, 436.
 2. U. S. P. 1008383; abst. J. S. C. I. 1911, **30**, 1450; C. A. 1912, **6**, 195. F. DuPont, E. P. 17038, 1912; F. P. 446269, 1912; abst. J. S. C. I. 1913, **32**, 141, 487; C. A. 1914, **8**, 302.
 3. U. S. P. 1242264, 1917; abst. J. S. C. I. 1917, **36**, 1235.
 4. Norw. P. 16083; abst. Mon. Sci. 1908, **69**, 109. A. Grau and F. Russ, U. S. P. 884919, 884920; abst. J. S. C. I. 1908, **27**, 501; Mon. Sci. 1909, **71**, 29; Chem. Ztg. Rep. 1908, **32**, 301. O. Gallander and E. Prytz, Norw. P. 28210, 1917; abst. C. A. 1919, **13**, 250. J. Straub, D. R. P. 304002, 1915; abst. J. S. C. I. 1918, **37**, 370-A; Mon. Sci. 1918, **85**, 59; 1919, **87**, 21; Chem. Zentr. 1918, **89**, 587; Chem. Ztg. Rep. 1918, **42**, 72. Elektrochem. Werke. E. P. 388305, 1908; abst. J. S. C. I. 1908, **27**, 939; Mon. Sci. 1909, **71**, 10; Chem. Ztg. Rep. 1908, **32**, 452.
 5. E. P. 605, 1909; abst. J. S. C. I. 1909, **28**, 1145.
 6. E. P. 9703, 1904; abst. J. S. C. I. 1905, **24**, 341. Lewis, E. P. Appl. 18473, 1916; J. S. C. I. 1917, **36**, 2. J. Sockett, E. P. 671, 1911; abst. C. A. 1912, **6**, 1735; J. S. C. I. 1912, **31**, 178. N. Busvold, U. S. P. 1222928, 1917; abst. J. S. C. I. 1917, **36**, 646.
 7. U. S. P. 1253534; abst. C. A. 1918, **12**, 747; J. S. C. I. 1918, **37**, 150-A; addn. dated April 17, 1914 to F. P. 453845, 1913; abst. J. S. C. I. 1915, **34**, 552; Chem. Ztg. Rep. 1913, **37**, 474.
 8. E. P. 2181, 1874. R. Drawe, U. S. P. 1283112, 1918; abst. C. A. 1919, **13**, 168. P. Winand, U. S. P. 1059581, 1913; J. S. C. I. 1913, **32**, 601; C. A. 1913, **7**, 2110; Chem. Ztg. Rep. 1913, **37**, 345. Atmospheric Products Co., E. P. 14781, 1902; abst. J. S. C. I. 1902, **21**, 1282. Nobel's Explosives Co. and D. Cross, E. P. 21607, 1910; 9682, 1911; abst. J. S. C. I. 1911, **30**, 1211; C. A. 1912, **6**, 1406; Chem. Ztg. Rep. 1912, **36**, 170.
 9. Dan. P. 21232, 1916; abst. C. A. 1916, **10**, 2391.
 10. E. P. 22037, 1909; abst. J. S. C. I. 1910, **29**, 211; Chem. Ztg. Rep. 1911, **35**, 54.
 11. E. P. 26499, 1913; abst. J. S. C. I. 1915, **34**, 872. Belg. P. 261929, 262377, 1913; Swiss P. 74128, 1917; F. P. 465045; D. R. P. July 26, 1913; abst. C. A. 1914, **8**, 3356; Chem. Ztg. Rep. 1914, **38**, 479; abst. J. S. C. I. 1914, **33**, 549. See also R. von Berneck, Can. P. 142468 and 142469; abst. C. A. 1913, **7**, 224. M. Moest, Can. P. 142470; abst. C. A. 1913, **7**, 224.

compounds of N and O at high temperatures and various pressures by burning fuel in the presence of N and O assisted by the oxides of chromium, titanium and uranium. The O. Bruenler process is similar.¹ According to T. Schloesing, who has patented a process for so doing,² and the analogous methods of W. Donald,³ E. Turpin,⁴ O. Loiseau,⁵ and R. Laing and G. Cossins,⁶ oxides of nitrogen are absorbed at temperatures of 300°–400° from the nitrous vapors issuing from the gases used in the absorption of sulfuric acid, and are re-oxidized to more available forms.

In the synthesis of nitric products by means of electric discharges in gaseous mixtures,⁷ several discharging sections are introduced into one and the same circuit in derivation. Similar exothermic reactions, as the oxidation of nitrogen, may be induced by supplying preheated gas to the heating zone of a furnace, and independently arranging around such zone, cooler gas adapted to flow in the same direction as the preheated gas.⁸ Embodying general ideas similar to those previously mentioned for the production of the oxides of nitrogen and their further transformation by processes of oxidation, are patents of C. Krauss and P. Staehelin,⁹ L. Basset,¹⁰ O. Carlson,¹¹ O. Engels and F. Duerre,¹²

Canada Explosives Co., Can. P. 142472; abst. 1913, **7**, 224. R. v. Berneck, M. Moest and H. Graf, U. S. P. 1021234, abst. C. A. 1912, **6**, 1345; Mon. Sci. 1912, **77**, 132.

1. U. S. P. 898033, 1908; abst. C. A. 1909, **3**, 362; Mon. Sci. 1909, **71**, 114; J. S. C. I. 1908, **27**, 982; E. P. 5901, 1906; abst. J. S. C. I. 1906, **25**, 811.

2. E. P. 643, 1878. F. P. 460328; abst. Chem. Ztg. Rep. 1914, **38**, 430.

3. E. P. 62, 1887; abst. Chem. Centr. 1888, **59**, 360.

4. E. P. 4544, 1881.

5. Swiss P. 44369, 1908.

6. E. P. 1819, 1861.

7. J. Kowalski and I. Moscicki, E. P. 20497, 1903; abst. J. S. C. I. 1903, **22**, 1297. U. S. 754147, 1904; abst. Mon. Sci. 1904, **61**, 128; Chem. Zts. 1904, **3**, 545.

8. E. P. 14528, 1911; abst. C. A. 1913, **7**, 222; J. S. C. I. 1912, **31**, 490. F. P. 435733. U. S. P. 1065144; abst. J. S. C. I. 1912, **31**, 385, 490; C. A. 1913, **7**, 2676.

9. E. P. 26499, 1913; abst. J. S. C. I. 1915, **34**, 872. D. Donnachig, E. P. 24332, 1903; abst. J. S. C. I. 1904, **23**, 983.

10. E. P. 21475, 1907; abst. J. S. C. I. 1908, **27**, 906.

11. E. P. Appl. 2386, 1918; abst. J. S. C. I. 1918, **37**, A, 111.

12. D. R. P. 229096; abst. J. S. C. I. 1911, **30**, 84; Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1911, **82**, I, 177; Chem. Ztg. Rep. 1910, **34**, 632; Chem. Zts. 1911, **10**, No. 2260; Zts. ang. Chem. 1911, **24**, 87; Zts. Schéiss. Spreng. 1910, **5**, 481.

R. Esnault-Pelterie,¹ A. Foss,² L. Frederick,³ D. Helbig,⁴ K. Kaiser,⁵ C. von Koch,⁶ W. Landis,⁷ I. Moscicki,⁸ H. Niedenfuchr,⁹ O. Guttmann,¹⁰ H. Pfennig'sche,¹¹ W. Ramsay,¹² H. Rankin,¹³ Scherfenberg & Prager,¹⁴ K. von Vietinghoff-Scheel,¹⁵ and others.¹⁶

1. E. P. 100275; abst. C. A. 1916, **10**, 2130.
2. U. S. P. 1200334, 1916; abst. C. A. 1916, **10**, 3140; J. S. C. I. 1916, **35**, 1156.
3. E. P. 319, 403, 1911; abst. J. S. C. I. 1911, **30**, 684; C. A. 1911, **5**, 3136; Chem. Ztg. Rep. 1911, **35**, 392. E. P. 27558, 1910; abst. J. S. C. I. 1911, **30**, 1211; C. A. 1912, **6**, 1506. E. P. 4268, 1911; abst. J. S. C. I. 1911, **30**, 1211. F. P. 404230; abst. J. S. C. I. 1910, **29**, 211; F. P. 404720; abst. J. S. C. I. 1910, **29**, 211; F. P. 421022; abst. J. S. C. I. 1911, **30**, 541; Mon. Sci. 1913, **79**, 114. F. P. 421313; abst. J. S. C. I. 1911, **30**, 542, 620; C. A. 1912, **6**, 1968; Chem. Ztg. Rep. 1911, **35**, 305. F. P. 424598; abst. J. S. C. I. 1911, **30**, 684; C. A. 1912, **6**, 1969; Mon. Sci. 1913, **79**, 118; Chem. Ztg. Rep. 1911, **35**, 303. Swiss P. 50365 and 54253, addn. thereto.
4. E. P. 27790, 1907; abst. J. S. C. I. 1908, **27**, 817; F. P. 385193, 1907; abst. J. S. C. I. 1908, **27**, 576.
5. E. P. 12229, 20325, 1910; abst. C. A. 1911, **4**, 2919; 1916, **10**, 806; J. S. C. I. 1910, **29**, 1306, 1377, 1380; 1911, **30**, 130; F. P. 350966, 1904; 415976, 419782, 1910; abst. J. S. C. I. 1910, **29**, 1306; 1911, **30**, 130; D. R. P. 181657, 1904; U. S. P. 984925; abst. Zts. ang. Chem. 1905, **18**, 1762; Chem. Ztg. 1916, **40**, 14.
6. F. P. 435733, 1911; abst. J. S. C. I. 1912, **31**, 385. See C. Ellis, U. S. P. 1002249, 1911; abst. J. S. C. I. 1911, **30**, 1160; U. S. P. 1007683, 1184839; abst. J. S. C. I. 1911, **30**, 1382; 1916, **35**, 737.
7. U. S. P. 1242953, 1917; abst. J. S. C. I. 1917, **36**, 1234.
8. E. P. 3583, 1906; abst. C. A. 1907, **1**, 1462; J. S. C. I. 1907, **26**, 261. F. P. 369387; abst. J. S. C. I. 1907, **26**, 157; Mon. Sci. 1908, **69**, 76; 1911, **75**, 571. E. P. 4353, 1905; abst. J. S. C. I. 1905, **24**, 1012.
9. D. R. P. 155095; abst. Mon. Sci. 1905, **63**, 51; Chem. Centr. 1904, **75**, II, 1268; Chem. Ztg. Rep. 1904, **28**, 1028; Chem. Zts. 1905, **4**, No. 123; Jahr. Chem. 1904, **57**, 490; Wag. Jahr. 1904, **50**, I, 337; Zts. ang. Chem. 1905, **18**, 105.
10. D. R. P. 160709; abst. Chem. Centr. 1905, **76**, II, 89; Chem. Ztg. Rep. 1905, **29**, 695; Chem. Zts. 1906, **5**, No. 59; Zts. ang. Chem. 1905, **18**, 1713.
11. D. R. P. 229142, 1907; abst. C. A. 1911, **5**, 2313; Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1911, **82**, I, 177; Chem. Ztg. Rep. 1911, **35**, 11; Chem. Zts. 1911, **10**, No. 2285; Wag. Jahr. 1911, **57**, I, 464; Zts. ang. Chem. 1911, **24**, 37.
12. E. P. 26981, 1907; abst. C. A. 1909, **3**, 2493; J. S. C. I. 1909, **28**, 569.
13. U. S. P. 1150786, 1915; abst. C. A. 1915, **9**, 2699; J. S. C. I. 1915, **34**, 960.
14. D. R. P. 202560, 1907; abst. J. S. C. I. 1909, **28**, 90; Mon. Sci. 1911, **75**, 123; Chem. Zentr. 1908, **79**, II, 1549; Chem. Ztg. Rep. 1908, **32**, 572; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1908, **54**, I, 425; Zts. ang. Chem. 1908, **21**, 2578; Zts. Schiess. Spreng. 1908, **3**, 416.
15. D. R. P. 225706, 1908; abst. J. S. C. I. 1910, **29**, 1377; Mon. Sci. 1914, **81**, 149; Chem. Zentr. 1910, **81**, II, 1007; Chem. Ztg. Rep. 1910, **34**, 498; Chem. Zts. 1910, **9**, No. 2130; Jahr. Chem. 1910, **63**, II, 185; Wag. Jahr. 1910, **56**, I, 473; Zts. ang. Chem. 1910, **23**, 2189.
16. M. Moest and R. von Berneck, E. P. 19032, 1911; abst. C. A. 1913, **7**, 540; J. S. C. I. 1911, **30**, 1381; J. Soc. Dyers Col. 1911, **27**, 240. U. S. P. 1049754, 1913; abst. J. S. C. I. 1913, **32**, 142; C. A. 1913, **7**, 871; Mon. Sci. 1913, **79**, 99. Farb. Meister, Lucius u. Brüning, E. P. 3662, 1913; 9974

G. Taylor, J. Capps and A. Coolidge¹ have recorded detailed experimental studies on the production of nitric acid from nitrogen oxides; H. Rousset² has prepared a historical article on the manufacture of nitrogen compounds by biological methods, while P. Ray, M. Dey and J. Ghosh³ have studied the velocity of decomposition and dissociation constants of nitrous acid. E. Briner and E. Durand⁴ have investigated the conditions of formation of nitrous and nitric acids from nitrogen oxides and water by employing the laws of mass action at widely varying limits of pressure and temperature. Haueser⁵ has experimented upon the combustion of nitrogen by oxidizing gas mixtures, coupled with sudden cooling. The electrothermic combustion of atmospheric nitrogen has been made the subject of a critical study by F.

13842, 1914; 28738, 1915; abst. C. A. 1914, **8**, 2607; 1915, **9**, 2801; J. S. C. I. 1913, **32**, 1611; 1915, **34**, 872, 962. F. P. 153845; abst. J. S. C. I. 1913, **32**, 791. F. Forster and M. Koch, Zts. ang. Chem. 1908, 2161, 2209. A. Grau and F. Russ, Chem. Zentr. 1907, **78**, I, 1172. O. Dieffenbach and W. Moldenhauer, E. P. 8768, 1908; abst. J. S. C. I. 1909, **28**, 90; F. P. 389500, 1908; abst. J. S. C. I. 1908, **27**, 981; Mon. Sci. 1909, **71**, 112. M. LeBlanc and W. Nuranen, Zts. Elektrochem. 1906, **13**, 541. G. Lunge and E. Berl, Zts. ang. Chem. 1906, **19**, 811, 861; 1907, **20**, 1716. Norske Kvalstoffkompani, E. P. 6265, 1905. L. Friderich, Swiss P. 56365, 54253, 1910. F. Raschig, Zts. ang. Chem. 1905, **18**, 1281. Soc. L'Air Liquid (Soc. Anon. pour l'Etude et l'Exploitation des Procédés G. Claude, E. P. 18475, 1910; abst. Chem. Ztg. Rep. 1912, **36**, 19. R. Delplace, E. P. 431125, 1910; abst. Mon. Sci. 1913, **79**, 128. C. Vautin, E. P. 3939, 1909; abst. C. A. 1911, **5**, 161; J. S. C. I. 1910, **29**, 423. Westdeutsche Thomasphosphat-Werke Ges. E. P. 7829, 1906; 9639, 1907; abst. J. S. C. I. 1907, **26**, 475, 1238. F. P. 377199, 1907; abst. C. A. 1909, **3**, 105; J. S. C. I. 1907, **26**, 475; Chem. Ztg. Rep. 1907, **31**, 472. H. Neuberger, Zts. ang. Chem. 1905, **18**, 1761, 1810, 1843; 1906, **19**, 977. P. Winand, D. P. 186333; abst. C. A. 1908, **2**, 166; Mon. Sci. 1909, **71**, 153; Chem. Zentr. 1907, **78**, II, 756; Chem. Ztg. Rep. 1907, **31**, 339; Jahr. Chem. 1905-1908, I, 1785; Wag. Jahr. 1907, **53**, I, 410; Zts. ang. Chem. 1908, **21**, 797; Zts. Schiess. Spreng. 1907, **2**, 355. M. Bodenstein, Zts. ang. Chem. 1909, **22**, 1151. H. Wislicenus, Zts. ang. Chem. 1902, **15**, 50. E. Ludwig, Ber. 1868, **1**, 232. P. Presser, U. S. P. 898346. E. P. 20697, 1907; 7319, 1910; abst. J. S. C. I. 1908, **27**, 1058; 1910, **29**, 1157. M. Prentice, E. P. 1811, 1874. F. Haber and A. Koenig, Zts. Elektrochem. 1907, **13**, 725. O. Baudisch and G. Klinger, Ber. 1912, **45**, 3231.

1. J. Ind. Eng. Chem. 1918, **10**, 270; abst. C. A. 1918, **12**, 1109.

2. Rev. gén. chim. 1915, **18**, 95, 143; 1916, **19**, 16; abst. C. A. 1916, **10**, 1914.

3. Trans. Chem. Soc. 1917, **111**, 413; abst. J. S. C. I. 1917, **36**, 1175. See also E. Werner, J. S. C. I. 1917, **36**, 1147.

4. Compt. rend. 1912, **155**, 582, 1495.

5. Zts. Ver. Deut. Ingen. 1912, 1157; Zts. Elektrochem. 1906, 444; Chem. Trade J. 1914, **55**, 46. M. Platsch, D. R. P. 200138; abst. J. S. C. I. 1908, **27**, 940; Chem. Ztg. Rep. 1908, **32**, 438; Mon. Sci. 1911, **75**, 87; Chem. Zentr. 1908, **79**, II, 356; Jahr. Chem. 1905-1908, I, 1771; Wag. Jahr. 1908, **54**, I, 416; Zts. ang. Chem. 1908, **21**, 1850; Zts. Schiess. Spreng. 1908, **3**, 334.

Howles,¹ working independently, and also with A. McDougall.²

1. J. S. C. I. 1907, **26**, 290; abst. C. A. 1907, **1**, 2162.
2. J. C. S. 1900, **78**, ii, 651. See also F. Lepel, Ber. 1897, **30**, 1027; 1903, **36**, 439. Compare also J. Plücker, Pogg. Ann. 1861, **133**, 252. Lehmann, Die Elektrischen Lichterscheinungen und Entladungen, 1898, 353. A. Bonna, A. Le Royer and P. van Berchem, D. R. P. 93592, 1896; abst. Zts. ang. Chem. 1897, **10**, 596; Chem. Centr. 1897, **68**, II, 1084; Chem. Ztg. Rep. 1897, **21**, 791; Wag. Jahr. 1897, **43**, 408. For clarifying beer with small quantities of oxides of nitrogen see E. P. 5339, 1911; abst. C. A. 1912, **6**, 2483; J. S. C. I. 1911, **30**, 1320. See W. Borchers and E. Beck, D. R. P. 196323, abst. J. S. C. I. 1908, **27**, 576; Mon. Sci. 1911, **75**, 58; Chem. Zentr. 1908, **1**, **79**, 1341; Chem. Ztg. Rep. 1908, **32**, 245; Jahr. Chem. 1905-1908, **1**, 1721; Wag. Jahr. 1908, **54**, **1**, 465; Zts. ang. Chem. 1908, **21**, 1521. F. Gerhardt, Swiss P. 78272, 1918. E. Briner and N. Boubnoff, Compt. rend. 1913, **156**, 228. J. Moscicki, E. P. 13250, 1913; abst. C. A. 1914, **8**, 3762; J. S. C. I. 1914, **33**, 755. U. S. P. 1201607; abst. J. S. C. I. 1916, **35**, 1224. E. P. 458630; abst. J. S. C. I. 1913, **32**, 1076. L. Gerstenlryger, Belg. P. 217316, 1909. O. Gethmann and N. Cleiren, Belg. P. 254480, 1913. For German patents for the manufacture of Nitrogen Oxides, compare, 362, 13913, 18486, abst. Wag. Jahr. 1882, **28**, 1059. 19576, abst. Mon. Sci. 1883, **25**, 335; Wag. Jahr. 1883, **29**, 389. 20722, abst. Mon. Sci. 1883, **25**, 685; 1906, **65**, 336; Wag. Jahr. 1883, **29**, 377. 71279, abst. Ber. 1893, **26**, 1023; Chem. Centr. 1894, **65**, **1**, 61; Jahr. Chem. 1894, **47**, 438; Wag. Jahr. 1893, **39**, 423; Zts. ang. Chem. 1893, **6**, 612. 85103, abst. Chem. Centr. 1896, **67**, **1**, 1216; Chem. Ztg. 1896, **20**, 204; Jahr. Chem. 1896, **49**, 414; Wag. Jahr. 1896, **42**, 410; Zts. ang. Chem. 1896, **9**, 75. 174564, abst. Mon. Sci. 1908, **69**, 157; Chem. Centr. 1906, **77**, **11**, 1091; Chem. Ztg. Rep. 1906, **30**, 339; Jahr. Chem. 1905-1908, **1**, 1764. 179288, abst. Mon. Sci. 1909, **71**, 74; Chem. Zentr. 1907, **78**, **1**, 430; Chem. Ztg. Rep. 1907, **30**, **11**; Chem. Zts. 1907, **6**, 258; Jahr. Chem. 1905-1908, **1**, 1764; Wag. Jahr. 1906, **52**, **1**, 456; Zts. ang. Chem. 1907, **20**, 761. 182297, abst. Mon. Sci. 1909, **71**, 154; Chem. Zentr. 1907, **78**, **1**, 1558; Chem. Ztg. Rep. 1907, **31**, 140; Jahr. Chem. 1905-1908, **1**, 1773; Wag. Jahr. 1907, **53**, **1**, 408; Zts. ang. Chem. 1907, **20**, 1376; Zts. Schiess. Spreng. 1907, **2**, 116. 185094, abst. Mon. Sci. 1909, **71**, 66; Chem. Zentr. 1907, **78**, **11**, 653; Chem. Ztg. Rep. 1907, **31**, 309; Jahr. Chem. 1905-1908, **1**, 1774; Wag. Jahr. 1907, **53**, **1**, 405; Zts. ang. Chem. 1908, **21**, 798; Zts. Schiess. Spreng. 1907, **2**, 215. 186333, abst. Mon. Sci. 1909, **71**, 153; Chem. Zentr. 1907, **78**, **11**, 756; Chem. Ztg. Rep. 1907, **31**, 339; Jahr. Chem. 1905-1908, **1**, 1785; Wag. Jahr. 1907, **53**, **1**, 410; Zts. ang. Chem. 1908, **21**, 797; Zts. Schiess. Spreng. 1907, **2**, 355. 186464, 187367, abst. Chem. Zentr. 1907, **78**, **11**, 1281; Chem. Ztg. Rep. 1907, **31**, 454; Chem. Zts. 1907, **6**, No. 188; Jahr. Chem. 1905-1908, **1**, 1768; Wag. Jahr. 1907, **53**, **1**, 388; Zts. ang. Chem. 1908, **21**, 558. 189864, abst. Chem. Zentr. 1907, **78**, **11**, 1953; Chem. Ztg. Rep. 1907, **31**, 585; Chem. Zts. 1907, **6**, No. 434; Jahr. Chem. 1905-1908, **1**, 1769; Wag. Jahr. 1907, **53**, **1**, 397; Zts. ang. Chem. 1908, **21**, 556. 192883, abst. Chem. Zentr. 1908, **79**, **1**, 316; Chem. Ztg. Rep. 1908, **32**, 64; Chem. Zts. 1908, **7**, 615; Jahr. Chem. 1905-1908, **1**, 1774; Zts. ang. Chem. 1908, **21**, 797. 193402, abst. Chem. Zentr. 1908, **79**, **1**, 316; Chem. Ztg. Rep. 1908, **32**, 41; Jahr. Chem. 1905-1908, **1**, 1769; Zts. ang. Chem. 1908, **21**, 412. 193696, abst. Chem. Zentr. 1908, **79**, **1**, 317; Chem. Ztg. Rep. 1908, **32**, 50; Chem. Zts. 1908, **7**, 682; Jahr. Chem. 1905-1908, **1**, 1785; Zts. ang. Chem. 1908, **21**, 412. 194326, abst. Chem. Zentr. 1908, **79**, **1**, 908; Chem. Zts. 1908, **7**, 707; Jahr. Chem. 1905-1908, **1**, 1770; Wag. Jahr. 1908, **54**, **1**, 414; Zts. ang. Chem. 1908, **21**, 797. 196112, abst. Mon. Sci. 1911, **75**, 58; Chem. Zentr. 1908, **79**, **1**, 1220; Chem. Zts. 1908, **7**, 719; Jahr. Chem. 1905-1908, **1**, 1791; 1909, **62**, **1**, 534; Wag. Jahr. 1908, **54**, **1**, 424; Zts. ang. Chem. 1908, **21**, 1084; Zts. Schiess. Spreng. 1908, **3**, 194. 196113, abst. Mon. Sci. 1911, **75**, 58; Chem. Zentr. 1908, **79**, **1**, 1340; Chem.

As the culmination of the work of these investigators it was full:

Ztg. Rep. 1908, **32**, 252; Jahr. Chem. 1905-1908, **I**, 1330; Wag. Jahr. 1908 **54**, **I**, 426; Zts. ang. Chem. 1908, **21**, 1368. 196144, 1906; abst. J. S. C. I. 1908, **27**, 576; Chem. Zentr. 1908, **79**, **I**, 1341; Chem. Ztg. Rep. 1908, **32**, 232; Chem. Zts. 1908, **7**, 760; Jahr. Chem. 1905-1908, **I**, 1770; Wag. Jahr. 1908, **54**, **I**, 422; Zts. ang. Chem. 1908, **21**, 1083; Schiess. Spreng. 1908, **3**, 194. 196829, abst. Mon. Sci. 1911, **75**, 59; Chem. Zentr. 1908, **79**, **I**, 1503; Chem. Ztg. Rep. 1908, **32**, 245; Chem. Zts. 1908, **7**, 846; Jahr. Chem. 1905-1908, **I**, 1770; Wag. Jahr. 1908, **54**, **I**, 412; Zts. ang. Chem. 1908, **21**, 1244; 199561, 1907; abst. Chem. Ztg. Rep. 1908, **32**, 438; J. S. C. I. 1908, **27**, 897; Mon. Sci. 1911, **75**, 51; Chem. Zentr. 1908, **79**, **I**, 272; Chem. Ztg. Rep. 1908, **32**, 389; Chem. Zts. 1908, **7**, 889; Jahr. Chem. 1905-1908, **I**, 1785; Wag. Jahr. 1908, **54**, **I**, 423; Zts. ang. Chem. 1908, **21**, 1851; Zts. Schiess. Spreng. 1908, **3**, 334. F. P. 388281, 1908; abst. J. S. C. I. 1908, **27**, 897; Mon. Sci. 1909, **71**, 110; Chem. Ztg. Rep. 1908, **32**, 452. D. R. P. 200138, 1907; abst. J. S. C. I. 1908, **27**, 856; Chem. Zentr. 1908, **79**, **II**, 356; Chem. Ztg. Rep. 1908, **32**, 438; Jahr. Chem. 1905-1908, **I**, 1771; Wag. Jahr. 1908, **54**, **I**, 416; Zts. ang. Chem. 1908, **21**, 1850; Zts. Schiess. Spreng. 1908, **3**, 334. 200876, abst. Chem. Zentr. 1908, **79**, **II**, 654; Chem. Ztg. Rep. 1908, **32**, 452; Jahr. Chem. 1905-1908, **I**, 1771; Wag. Jahr. 1908, **54**, **I**, 415; Zts. ang. Chem. 1908, **21**, 2042; Zts. Schiess. Spreng. 1908, **3**, 374. 203748, abst. Mon. Sci. 1912, **77**, 49; Chem. Zentr. 1908, **79**, **II**, 1655; Chem. Ztg. Rep. 1908, **32**, 623; Chem. Zts. 1908, **7**, 918; Jahr. Chem. 1905-1908, **I**, 1699; Wag. Jahr. 1908, **54**, **I**, 382; Zts. ang. Chem. 1908, **21**, 2472; Zts. Schiess. Spreng. 1908, **3**, 470. 204882, Mon. Sci. 1912, **77**, 50; Chem. Zentr. 1909, **81**, **I**, 323; Chem. Ztg. Rep. 1909, **33**, 12; Chem. Zts. 1909, **8**, 1087; Jahr. Chem. 1909, **62**, 511; Wag. Jahr. 1908, **54**, **I**, 492; Zts. ang. Chem. 1909, **22**, 457. 205018, abst. Mon. Sci. 1912, **77**, 50; Chem. Zentr. 1909, **81**, **I**, 324; Chem. Ztg. Rep. 1909, **33**, 7; Jahr. Chem. 1909, **62**, 534; Zts. ang. Chem. 1909, **22**, 208. 205351, abst. Mon. Sci. 1912, **77**, 50; Chem. Zentr. 1909, **81**, **I**, 599; Chem. Ztg. Rep. 1909, **33**, 53; Jahr. Chem. 1909, **62**, 534; Wag. Jahr. 1909, **55**, **I**, 410; Zts. ang. Chem. 1909, **22**, 362; Zts. Schiess. Spreng. 1909, **4**, 55. 206949, abst. Mon. Sci. 1912, **77**, 90; Chem. Zentr. 1909, **80**, **I**, 1127; Chem. Ztg. Rep. 1909, **33**, 137; Chem. Zts. 1909, **8**, 1184; Jahr. Chem. 1909, **62**, 531; Wag. Jahr. 1909, **55**, **I**, 417; Zts. ang. Chem. 1909, **22**, 551; Zts. Schiess. Spreng. 1909, **4**, 95. 207158, 209961, abst. Mon. Sci. 1912, **77**, 97; Chem. Zentr. 1909, **80**, **I**, 1783; Chem. Ztg. Rep. 1909, **33**, 311; Jahr. Chem. 1909, **62**, **I**, 534; Wag. Jahr. 1909, **55**, **I**, 405; Zts. ang. Chem. 1909, **22**, 1278; Zts. Schiess. Spreng. 1909, **4**, 234. 210167, abst. Mon. Sci. 1912, **77**, 97; Chem. Zentr. 1909, **80**, **II**, 77; Chem. Ztg. Rep. 1909, **33**, 314; Jahr. Chem. 1909, **62**, 535; Wag. Jahr. 1909, **55**, **I**, 416; Zts. ang. Chem. 1909, **22**, 1318; Zts. Schiess. Spreng. 1909, **4**, 235. 210324, abst. Mon. Sci. 1912, **77**, 100; Chem. Zentr. 1909, **80**, **II**, 159; Chem. Ztg. Rep. 1909, **33**, 330; Jahr. Chem. 1909, **62**, 530; Wag. Jahr. 1909, **55**, **I**, 402; Zts. ang. Chem. 1909, **22**, 1372. 212423, abst. Mon. Sci. 1912, **77**, 167; Chem. Zentr. 1909, **80**, **II**, 569; Chem. Ztg. Rep. 1909, **33**, 489; Chem. Zts. 1910, **9**, 1560; Jahr. Chem. 1909, **62**, **I**, 535; Wag. Jahr. 1909, **55**, **I**, 394; Zts. ang. Chem. 1909, **22**, 1811; Zts. Schiess. Spreng. 1909, **4**, 333. 212868, abst. Mon. Sci. 1912, **77**, 98; Chem. Zentr. 1909, **80**, **II**, 665; Chem. Ztg. Rep. 1909, **33**, 477; Chem. Zts. 1910, **9**, 1648; Jahr. Chem. 1909, **62**, **I**, 535; Wag. Jahr. 1909, **55**, **I**, 416; Zts. ang. Chem. 1909, **22**, 1811; Zts. Schiess. Spreng. 1909, **4**, 333. 216518, abst. Mon. Sci. 1913, **79**, 157; Chem. Zentr. 1910, **81**, **I**, 129; Chem. Ztg. Rep. 1910, **34**, 19; Chem. Zts. 1910, **9**, 1564; Jahr. Chem. 1909, **62**, **I**, 530; Wag. Jahr. 1909, **55**, **I**, 415; Zts. ang. Chem. 1910, **23**, 228; Zts. Schiess. Spreng. 1910, **5**, 11. 217079, abst. Mon. Sci. 1913, **79**, 157; Chem. Zentr. 1910, **81**, **I**, 307; Chem. Ztg. Rep. 1910, **34**, 63; Jahr. Chem. 1909, **62**, **I**, 530; Wag. Jahr. 1909, **55**, **I**, 413; Zts. ang. Chem. 1910, **23**, 380; Zts. Schiess. Spreng. 1910, **5**, 53. 217550, abst. Mon. Sci. 1913, **79**, 157; Chem. Zentr. 1910, **81**, **I**, 585; Chem.

demonstrated that the combustion of nitrogen to products of use-

Ztg. Rep. 1910, **34**, 84; Jahr. Chem. 1910, **63**, I, 584; Wag. Jahr. 1909, **55**, I, 414; Zts. ang. Chem. 1910, **23**, 380; Zts. Schiess. Spreng. 1910, **5**, 53. 218570, C. A. 1910, **4**, 1797; abst. Mon. Sci. 1913, **79**, 158; Chem. Zentr. 1910, **81**, I, 780; Chem. Ztg. Rep. 1910, **34**, 106; Chem. Zts. 1910, **9**, 1834; Jahr. Chem. 1910, **63**, 588; Wag. Jahr. 1910, **56**, I, 486; Zts. ang. Chem. 1910, **23**, 816; Zts. Schiess. Spreng. 1910, **5**, 115. 218671, 1908; abst. J. S. C. I. 1909, **28**, 656; Chem. Zentr. 1910, **81**, I, 781; Chem. Ztg. Rep. 1910, **34**, 107; Jahr. Chem. 1910, **63**, I, 548; Zts. ang. Chem. 1910, **23**, 762; Zts. Schiess. Spreng. 1910, **5**, 114. U. S. P. 1115164, 1914; abst. J. S. C. I. 1914, **33**, 1154. D. R. P. 218813, C. A. 1910, **4**, 1943; Zts. ang. Chem. 1910, **23**, 763; Mon. Sci. 1913, **79**, 158; Chem. Zentr. 1910, **81**, I, 876; Chem. Ztg. Rep. 1910, **34**, 151; Jahr. Chem. 1910, **63**, I, 583; Wag. Jahr. 1910, **56**, I, 475; Zts. Schiess. Spreng. 1910, **5**, 175. 219494, abst. Chem. Zentr. 1910, **81**, I, 971; Chem. Ztg. Rep. 1910, **34**, 142; Chem. Zts. 1910, **9**, 1924; Jahr. Chem. 1910, **63**, I, 584; Wag. Jahr. 1910, **56**, I, 471; Zts. ang. Chem. 1910, **23**, 1049; Zts. Schiess. Spreng. 1910, **5**, 175. 220539, abst. Mon. Sci. 1914, **81**, 76; Chem. Zentr. 1910, **81**, I, 1397; Chem. Ztg. Rep. 1910, **34**, 179; Chem. Zts. 1910, **9**, 1876; Jahr. Chem. 1910, **63**, I, 588; Wag. Jahr. 1910, **56**, I, 480; Zts. ang. Chem. 1910, **23**, 1050; Zts. Schiess. Spreng. 1910, **5**, 175. 222629, abst. Mon. Sci. 1914, **81**, 77; Chem. Zentr. 1910, **81**, II, 120; Chem. Ztg. Rep. 1910, **34**, 297; Wag. Jahr. 1910, **56**, I, 474; Zts. ang. Chem. 1910, **23**, 1736; Zts. Schiess. Spreng. 1910, **5**, 297. 223026, abst. Mon. Sci. 1914, **81**, 77; Chem. Zentr. 1910, **81**, II, 253; Chem. Ztg. Rep. 1910, **34**, 342; Jahr. Chem. 1910, **63**, I, 588; Wag. Jahr. 1910, **56**, I, 481; Zts. ang. Chem. 1910, **23**, 1961; Zts. Schiess. Spreng. 1910, **5**, 257. 223556, abst. Mon. Sci. 1914, **81**, 78; Chem. Zentr. 1910, **81**, II, 427; Chem. Ztg. Rep. 1910, **34**, 342; Chem. Zts. 1910, **9**, 2027; Jahr. Chem. 1910, **63**, I, 588; Wag. Jahr. 1910, **56**, I, 481; Zts. ang. Chem. 1910, **23**, 1901; Zts. Schiess. Spreng. 1910, **5**, 297. 223887, abst. Mon. Sci. 1914, **81**, 87; Chem. Zentr. 1910, **81**, II, 511; Chem. Ztg. Rep. 1910, **34**, 425; Jahr. Chem. 1910, **63**, I, 583; Wag. Jahr. 1910, **56**, I, 466; Zts. ang. Chem. 1910, **23**, 2292. 224329, abst. Chem. Zentr. 1910, **81**, II, 511; Chem. Ztg. Rep. 1910, **34**, 397; Jahr. Chem. 1910, **63**, I, 587; Zts. ang. Chem. 1910, **23**, 2098; Zts. Schiess. Spreng. 1910, **5**, 338. 225153, abst. Chem. Zentr. 1910, **81**, II, 1103; Chem. Ztg. Rep. 1910, **34**, 498; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 487; Zts. ang. Chem. 1910, **23**, 2189. 225239, abst. Mon. Sci. 1914, **81**, 87; Chem. Zentr. 1910, **81**, II, 1007; Chem. Ztg. Rep. 1910, **34**, 510; Jahr. Chem. 1910, **63**, I, 583; Wag. Jahr. 1910, **56**, I, 468; Zts. ang. Chem. 1910, **23**, 2189. 225706, 1908; abst. J. S. C. I. 1910, **29**, 1377; Mon. Sci. 1914, **81**, 87; Chem. Zentr. 1910, **81**, II, 1007; Chem. Ztg. Rep. 1910, **34**, 498; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 473; Zts. ang. Chem. 1910, **23**, 2189; Zts. Schiess. Spreng. 1910, **5**, 359. 226867, abst. Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1910, **81**, II, 1345; Chem. Ztg. Rep. 1910, **34**, 543; Jahr. Chem. 1910, **63**, I, 580; Wag. Jahr. 1910, **56**, I, 477; Zts. ang. Chem. 1910, **23**, 2292. 227012, 1908; abst. J. S. C. I. 1910, **29**, 1378; Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1910, **81**, II, 1419; Chem. Ztg. Rep. 1910, **34**, 543; Jahr. Chem. 1910, **63**, I, 583; Wag. Jahr. 1910, **56**, I, 459; Zts. ang. Chem. 1910, **23**, 2337; Zts. Schiess. Spreng. 1910, **5**, 441. 227490, abst. Mon. Sci. 1914, **81**, 85; Chem. Zentr. 1910, **81**, II, 1419; Chem. Ztg. Rep. 1910, **34**, 550; Jahr. Chem. 1910, **63**, I, 584; Wag. Jahr. 1910, **56**, I, 477; Zts. ang. Chem. 1910, **23**, 2292; Zts. Schiess. Spreng. 1910, **5**, 442. 228426, abst. Mon. Sci. 1914, **81**, 85; Chem. Zentr. 1910, **81**, II, 1694; Chem. Ztg. Rep. 1910, **34**, 581; Jahr. Chem. 1910, **63**, 585; Wag. Jahr. 1910, **56**, I, 479; Zts. ang. Chem. 1910, **23**, 2337; Zts. Schiess. Spreng. 1910, **5**, 481. 229142, abst. Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1911, **82**, I, 177; Chem. Ztg. Rep. 1911, **35**, 11; Chem. Zts. 1911, **10**, 2285; Wag. Jahr. 1911, **57**, I, 464; Zts. ang. Chem. 1911, **24**, 87; Zts. Schiess. Spreng. 1911, **6**, 96. 229780, abst. Mon. Sci. 1914, **81**, 84; Chem. Zentr. 1911, **82**, I, 274; Chem. Ztg.

fulness in the arts, was a problem offering successful solution.

Rep. 1911, **35**, 43; Chem. Zts. 1911, **10**, 2373; Zts. ang. Chem. 1911, **24**, 281. 230042, abst. Mon. Sci. 1914, **81**, 84; Chem. Zentr. 1911, **82**, I, 357; Chem. Ztg. Rep. 1911, **35**, 66; Wag. Jahr. 1911, **57**, I, 465; Zts. ang. Chem. 1911, **24**, 281; Zts. Schiess. Spreng. 1911, **6**, 157. 230170; abst. Mon. Sci. 1914, **81**, 84; Chem. Zentr. 1911, **82**, I, 357; Chem. Ztg. Rep. 1911, **35**, 66; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 281; Zts. Schiess. Spreng. 1911, **6**, 75. 231546, abst. Mon. Sci. 1915, **82**, 56; Chem. Zentr. 1911, **82**, I, 567; Chem. Ztg. Rep. 1911, **35**, 111; Chem. Zts. 1911, **10**, 2501; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 565; Zts. Schiess. Spreng. 1911, **6**, 157. 231805, abst. Chem. Zentr. 1911, **82**, I, 852; Chem. Ztg. Rep. 1911, **35**, 127; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 565. 232569, 1907; abst. Chem. Zentr. 1911, **82**, I, 1018; Chem. Ztg. Rep. 1911, **35**, 180; Wag. Jahr. 1911, **57**, I, 464; Zts. ang. Chem. 1911, **24**, 855; C. A. 1911, **5**, 2709. See also D. R. P. 218813. 232926, abst. Chem. Zentr. 1911, **82**, I, 1089; Chem. Ztg. Rep. 1911, **35**, 223; Chem. Zts. 1912, **11**, 2621; Wag. Jahr. 1911, **57**, I, 467; Zts. ang. Chem. 1911, **24**, 856; Zts. Schiess. Spreng. 1911, **6**, 156. 233729, 1910; abst. Chem. Zentr. 1911, **82**, I, 1388; Chem. Ztg. Rep. 1911, **35**, 271; Wag. Jahr. 1911, **57**, I, 466; Zts. ang. Chem. 1911, **24**, 949; Zts. Schiess. Spreng. 1911, **6**, 232; J. S. C. I. 1911, **30**, 747. 233967, abst. Chem. Zentr. 1911, **82**, I, 1466; Chem. Ztg. Rep. 1911, **35**, 234; Wag. Jahr. 1911, **57**, I, 467; Zts. ang. Chem. 1911, **24**, 1003; Zts. Schiess. Spreng. 1911, **6**, 232. 233982, abst. Chem. Zentr. 1911, **82**, I, 1466; Chem. Ztg. Rep. 1911, **35**, 262; Wag. Jahr. 1911, **57**, I, 467; Zts. Schiess. Spreng. 1911, **6**, 232. 235299, abst. Chem. Zentr. 1911, **82**, II, 111; Chem. Ztg. Rep. 1911, **35**, 342; Wag. Jahr. 1911, **57**, I, 464; Zts. ang. Chem. 1911, **24**, 1444; Zts. Schiess. Spreng. 1911, **6**, 334. 237562; abst. C. A. 1912, **6**, 1508; Chem. Zentr. 1911, **82**, II, 812; Chem. Ztg. Rep. 1911, **35**, 168; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 1782; Zts. Schiess. Spreng. 1911, **6**, 354. 237796, abst. C. A. 1912, **6**, 1575; Chem. Zentr. 1911, **82**, II, 920; Chem. Ztg. Rep. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 461; Zts. ang. Chem. 1911, **24**, 1883. 238369, abst. C. A. 1912, **6**, 1663; Chem. Zentr. 1911, **82**, II, 1067; Chem. Ztg. Rep. 1911, **35**, 529; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 2029; Zts. Schiess. Spreng. 1911, **6**, 411. 238569, abst. C. A. 1912, **6**, 1971; Chem. Zentr. 1911, **82**, II, 1184; Chem. Ztg. Rep. 1911, **35**, 524; Wag. Jahr. 1911, **57**, I, 426; Zts. ang. Chem. 1911, **24**, 2078. 242288, abst. C. A. 1912, **6**, 2153; Chem. Zentr. 1912, **83**, I, 296; Chem. Ztg. Rep. 1912, **36**, 43; Wag. Jahr. 1912, **58**, I, 415; Zts. ang. Chem. 1912, **25**, 328; Zts. Schiess. Spreng. 1912, **7**, 185. 243840, abst. C. A. 1912, **6**, 2299; Chem. Zentr. 1912, **83**, I, 865; Chem. Ztg. Rep. 1912, **36**, 156; Wag. Jahr. 1912, **58**, I, 417; Zts. ang. Chem. 1912, **25**, 596; Zts. Schiess. Spreng. 1912, **7**, 185. 244362, abst. C. A. 1912, **6**, 2213; Chem. Zentr. 1912, **83**, I, 958; Chem. Ztg. Rep. 1912, **36**, 203; Wag. Jahr. 1912, **58**, I, 416; Zts. ang. Chem. 1912, **25**, 748. 244840, abst. C. A. 1912, **6**, 2213; Chem. Zentr. 1912, **83**, I, 1162; Chem. Ztg. Rep. 1912, **36**, 234; Wag. Jahr. 1912, **58**, I, 419; Zts. ang. Chem. 1912, **25**, 858; Zts. Schiess. Spreng. 1912, **7**, 229. 245492, abst. C. A. 1912, **6**, 2502; Chem. Zentr. 1912, **83**, I, 1406; Chem. Ztg. Rep. 1912, **36**, 267; Wag. Jahr. 1912, **58**, I, 420; Zts. ang. Chem. 1912, **25**, 1141. 246615, abst. C. A. 1912, **6**, 2504; Chem. Zentr. 1912, **83**, I, 1872; Chem. Ztg. Rep. 1912, **36**, 302; Wag. Jahr. 1912, **58**, I, 421; Zts. ang. Chem. 1912, **25**, 1649. 246712, abst. C. A. 1912, **6**, 2504; Chem. Zentr. 1912, **83**, I, 1872; Chem. Ztg. Rep. 1912, **36**, 302; Wag. Jahr. 1912, **58**, I, 420; Zts. ang. Chem. 1912, **25**, 1648; Zts. Schiess. Spreng. 1912, **7**, 248. 248290, abst. C. A. 1912, **6**, 2678; Chem. Zentr. 1912, **83**, II, 208; Chem. Ztg. Rep. 1912, **36**, 405; Wag. Jahr. 1912, **58**, I, 385; Zts. ang. Chem. 1912, **25**, 1647. 249328, abst. C. A. 1912, **6**, 2984; Chem. Zentr. 1912, **83**, II, 464; Chem. Ztg. Rep. 1912, **36**, 462; Wag. Jahr. 1912, **58**, I, 416; Zts. ang. Chem. 1912, **25**, 1649. 249856, abst. C. A. 1912, **6**, 3170; Chem. Zentr. 1912, **83**, II, 651; Chem. Ztg. Rep.

Nitrogen Monoxide. Nitrous oxide, N_2O ,¹ is a pleasant

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ing zinc and other metals in dilute nitric acid;¹ by the decomposition of ammonium nitrate on heating;² by heating sodium nitrate to 240° with an excess of ammonium sulfate;³ and in great purity by allowing a quantity of the liquefied gas to evaporate partially, collecting the gas evolved from the residue, which is free from nitrogen.⁴

The specific gravity of this gas is 1.5297⁵ or 1.5301,⁶ and when liquefied, has a specific gravity at 0° of 0.9369,⁷ boils at -89.8° and freezes at -103.7°.⁸ Its critical temperature is given as 37°,⁹ 38.8°. Nitrous oxide has been prepared in the solid state like snow.¹⁰ Copper¹¹ and potassium¹² when strongly heated with nitrous oxide, are oxidized, nitrogen being formed. Nitrous oxide decomposes explosively under the impulse of a violent shock.¹³ Forms an unstable crystalline hydrate with water at low temperatures.¹⁴ R. Marston produces nitrous oxide¹⁵ by passing a

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10. T. Wills, J. C. S. 1874, **27**, 21. P. Guye and A. Pintza, Compt. rend. 1904, **139**, 677; 1905, **141**, 51.
11. P. Sabatier and J. Senderens, Compt. rend. 1895, **120**, 618, 1212; 1902, **135**, 278; abst. Bull. Soc. Chim. 1895, (3), **13**, 870; Jahr. Chem. 1895, **48**, 559, 560.
12. W. Holt and W. Sims, J. C. S. 1894, **65**, 432. J. Mills, J. Phys. Chem. 1906, **10**, 1.
13. L. Maquenne, Compt. rend. 1895, **121**, 424.
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15. E. P. 4080, 1899.

mixture of air and ammonia through a heated retort containing copper, reducing the oxides formed to nitrous oxide, by passing the gases over moist iron shavings. R. Piéret¹ has found that in a mixture of N and O, nitrous oxide is found in large amounts in certain points in a flame, and may be withdrawn from the hottest zone, with rapid cooling in order to prevent its decomposition.²

A. Warner³ purifies nitrous oxide by passing the gas successively into solutions of potassium permanganate, 10% NaOH and a solution containing 20% sulfuric acid.

- Nitrogen Dioxide.**⁴ Nitric Oxide,⁵ NO, Anhydride of Nitrous Oxide.
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 5. T. Andrews and P. Tait, Proc. Roy. Soc. 1860, **10**, 247; abst. Jahr. Chem. 1860, **13**, 31. H. Auden and G. Fowler, Chem. News, 1895, **72**, 163; abst. Jahr. Chem. 1895, **48**, 561. P. Austen, Am. Chem. J. 1889, **11**, 172; Chem. News, 1889, **59**, 208; Jahr. Chem. 1889, **42**, 333. H. Baker, Chem. News, 1894, **69**, 270; abst. Jahr. Chem. 1894, **47**, 297; J. C. S. 1894, **65**, 611. A. Balard, Ann. Chim. Phys. 1834, **57**, 225; abst. Ann. 1835, **14**, 167, 298. G. Baxter and C. Hickey, An. Chem. J. 1905, **33**, 300; abst. Chem. Centr. 1905, **76**, I, 1299. M. Berthelot, Compt. rend. 1873, **77**, 1448; abst. Jahr. Chem. 1874, **27**, 221. Compt. rend. 1876, **82**, 1360; abst. Jahr. Chem. 1876, **29**, 165; abst. Bull. Soc. Chim. 1876, (2), **26**, 101. Compt. rend. 1877, **85**, 1017; 1880, **90**, 779; 1881, **93**, 613; 1884, **98**, 545. Stat.

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copper foil or turnings;¹ by allowing a concentrated solution of sodium nitrite to drop into a HCl solution of a ferrous salt;² by mixing a ferrocyanide, nitrite and acetic acid;³ acting upon mercury with sulfuric and nitric acids;⁴ by electrolysis of dilute nitric acid;⁵ by employing around the reaction zone of an elec-

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5. Farbwerke vorm. Meister, Lucius and Brüning, F. P. 10522, 1911; abst. J. S. C. I. 1911, **32**, 955; C. A. 1911, **5**, 3328; E. P. 15948, 1911; abst. C. A. 1913, **7**, 223; J. S. C. I. 1912, **31**, 775; E. P. 19032, 1911; abst. J. S. C. I. 1911, **30**, 930, 1381; C. A. 1913, **7**, 540; J. Soc. Dyers Col. 1911, **27**, 240; U. S. P. 1049754, 1913; abst. J. S. C. I. 1913, **32**, 142; C. A. 1913, **7**, 871; Mon. Sci. 1913, **79**, 99. F. P. 428657; abst. J. S. C. I. 1911, **30**, 1161; Mon. Sci. 1913, **79**, 125; D. R. P. 244362; U. S. P. 1021234; abst. J. S. C. I. 1912, **31**, 386; C. A. 1912, **6**, 1345; Mon. Sci. 1912, **77**, 132; Aust. P. 59154. See also Farbwerke Höchst, F. P. 428657, 1911; abst. J. S. C. I. 1911, **30**, 1161; abst. C. A. 1912, **6**, 2213; Chem. Zentr. 1912, **83**, I, 958; Chem. Ztg. Rep. 1912, **26**, 203; Wag. Jahr. 1912, **58**, I, 416; Zts. ang. Chem. 1912, **25**, 748.

tric arc, an atmosphere rich in oxygen, and around this, one of atmospheric air;¹ or by the use of electrodes made of aluminium and iron.²

Nitric oxide is a colorless gas of sp. gr. 1.0387,³ while according to P. Guye,⁴ and P. Guye and C. Davila,⁵ one liter weighs 1.3402 gm., and boils at -153.6° .⁶ It forms a colorless liquid, colored blue by a trace of higher oxide,⁷ while according to J. Dewar⁸ the liquid is blue and the solid colorless. Does not combine with oxygen when both are dry,⁹ but combines explosively with liquid oxygen.¹⁰ Nitric oxide is extremely stable when heated,¹¹ decomposition being very slight at 900° . When exposed to a sharp shock¹² it is resolved into its elements.

Complete combustion of the gas takes place when it is passed with hydrogen through a heated platinum capillary tube,¹³ or over finely divided nickel above 180° .¹⁴

1. Norsk Hydroelektrisk Kvaestof Aktieselskab, U. S. P. 1111301; abst. C. A. 1914, **8**, 3536; Mon. Sci. 1914, **81**, 179.
2. C. Rossi, E. P. 23959, 1913; abst. J. S. C. I. 1914, **33**, 1154; F. P. 463821, 1913; abst. J. S. C. I. 1914, **33**, 421; C. A. 1914, **8**, 3103; Mon. Sci. 1916, **83**, 10; Chem. Ztg. Rep. 1914, **38**, 344.
3. A. Leduc, Compt. rend. 1893, **116**, 322. G. Dacomo and V. Meyer, Ann. 1887, **240**, 326. P. Guye and C. Davila, Compt. rend. 1905, **141**, 826. R. Gray, Proc. C. S. 1903, **19**, 66; Chem. Zentr. 1903, I, 912. G. Liveing and J. Dewar, Phil. Mag. 1892, (5), **34**, 205. A. Naumann, Ann. Suppl. 1867, **5**, 252. J. Jeans, Phil. Mag. 1894, (8), **8**, 692. J. Thomsen, Ber. 1880, **13**, 498. M. Berthelot, Compt. rend. 1880, **90**, 779. R. Threlfall, Phil. Mag. 1887, (5), **23**, 233; Jahr. Chem. 1887, **40**, 211.
4. Proc. Chem. Soc. 1903, **19**, 66.
5. Compt. rend. 1905, **141**, 826.
6. K. Olszewski, Compt. rend. 1885, **100**, 940.
7. Travers, "Exp. Study of Gases," 1901, 244.
8. J. Dewar, Proc. Chem. Soc. 1895, **11**, 225; Ber. 1885, **18**, 1384.
9. H. Baker, J. C. S. 1894, **65**, 613.
10. J. Dewar, Proc. Chem. Soc. 1895, **11**, 225.
11. F. Emich, Monatsh. 1892, **13**, 78, 615.
12. M. Berthelot, Compt. rend. 1881, **93**, 613.
13. G. Knorre and K. Arndt, Ber. 1899, **32**, 2136.
14. P. Sabatier and J. Senderens, Compt. rend. 1902, **135**, 278. See also H. Auden and G. Fowler, Chem. News, 1895, **72**, 163. E. Sell, Ber. 1874, **7**, 1522. E. Divers, J. C. S. 1899, **55**, 92. C. Oppenheimer, Ber. 1903, **36**, 1744. P. Sabatier and J. Senderens, Compt. rend. 1895, **120**, 1158. G. Dacomo and V. Meyer, Ann. 1887, **240**, 326. R. Pickett, E. P. 415594; abst. C. A. 1912, **6**, 1966; Mon. Sci. 1911, **75**, 573; 1913, **79**, 82; Chem. Ztg. Rep. 1910, **34**, 561. D. R. P. 226867; abst. J. S. C. I. 1910, **29**, 1250; Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1910, **81**, II, 1345; Chem. Ztg. Rep. 1910, **34**, 543; Jahr. Chem. 1910, **63**, I, 580; Wag. Jahr. 1910, **56**, I, 477; Zts. ang. Chem. 1910, **23**, 2292. H. Dixon and J. Peterkin, J. C. S. 1899, **75**, 613. K. Finkel and W. Nernst, Zts. anorg. Chem. 1905, **45**, 116; abst. J. S. C. I. 1905, **24**, 693; Zts. ang. Chem. 1905, **18**, 1773. For nitric oxide from internal combustion engines, see R. Drawe, U. S. P. 1283112, 1918; abst. C. A. 1919, **13**, 168. K. Jellinek, Zts. anorg. Chem. 1906, **49**, 229; abst. J. C. S. 1906,

Nitrogen Trioxide. Nitrous anhydride,¹ N_2O_3 , is formed when electric discharges are passed through liquid air;² when arsenious oxide is treated with nitric acid of sp. gr. 1.35, or starch by an acid of sp. gr. 1.33,³ nitrogen trioxide is evolved. It is completely absorbed by concentrated sulfuric acid, forming nitrosylsulfuric acid,⁴ and by sodium hydroxide solution, forming sodium nitrite.⁵ This oxide is also produced by the direct union of nitric oxide and solid nitrogen peroxide,⁶ and of oxygen with

90, ii, 437. For the rate of oxidation of NO, see E. Briner and E. Fridori, *Helvetica Chim. Acta*, 1918, **1**, 181; abst. C. A. 1919, **13**, 100. W. Nernst, *Zts. Elektrochem.* 1906, **12**, 527, 544; *Zts. anorg. Chem.* 1906, **49**, 213, 257. *Zts. Elektrochem.* 1907, **13**, 521; 1910, **16**, 96.

1. M. Berthelot, *Ann. Chim. Phys.* 1878, (5), **14**, 367; abst. *Jahr. Chem.* 1878, **31**, 221. *Compt. rend.* 1880, **90**, 779; abst. *Jahr. Chem.* 1880, **33**, 118. F. Bihlans, *Compt. rend.* 1889, **109**, 63; abst. *Jahr. Chem.* 1889, **42**, 402. D. Brewster, *Pogg. Ann.* 1833, **28**, 385. H. Dixon and J. Peterkin J. C. S. 1899, **75**, 613. P. Dulong and A. Petit, *Ann. Chim. Phys.* 1816, **2**, 240. L. Francesconi and N. Sciaccia, *Gaz. chim. ital.* 1904, **34**, i, 447; abst. *Chem. Centr.* 1904, **75**, 11, 397. E. Fremy, *Compt. rend.* 1870, **70**, 61; abst. *Jahr. Chem.* 1870, **23**, 272. J. Fritzsche, *J. prakt. Chem.* 1840, **19**, 179. R. Gaines, *Chem. News*, 1883, **48**, 97; abst. *Jahr. Chem.* 1883, **36**, 307. D. Gernez, *Compt. rend.* 1878, **86**, 1549; abst. *Jahr. Chem.* 1878, **31**, 21. A. Geuther, *Ann.* 1888, **245**, 96. A. Geuther and A. Michaelis, *Ber.* 1871, **4**, 766. R. Günsberg, *Wien. Akad. Ber.* 1873, **68**, 11, 498; abst. *Jahr. Chem.* 1873, **26**, 218. C. Hasenbach, *J. prakt. Chem.* 1871, **112**, 1; abst. *Am. J. Sci.* 1871, (3), **2**, 362; *Bull. Soc. Chim.* 1871, (2), **16**, 236; *Jahr. Chem.* 1871, **24**, 237. S. Helbig, *Atti. Acad. dei Lincei*, 1902, (5), **11**, 11, 57; 1903, **12**, I, 166. *Gaz. chim. ital.* 1903, **33**, 454. D. Huizinga, *Jahr. Chem.* 1867, **20**, 179; see also *Ann.* 1872, **161**, 232. B. Liljenstern and L. Marchlewski, *Zts. anor. Chem.* 1894, **5**, 288; abst. *Jahr. Chem.* 1894, **47**, 442. E. Luck, *Zts. anal. Chem.* 1869, **8**, 402; abst. *Jahr. Chem.* 1869, **22**, 183; *Chem. Centr.* 1870, **41**, 561. G. Lunge, *Ber.* 1878, **11**, 1229, 1641; 1879, **12**, 357; 1882, **15**, 495; 1885, **18**, 1376, 1384; abst. *Dingl. Poly.* 1879, **233**, 63. G. Lunge and G. Porschnew, *Zts. ang. Chem.* 1894, **7**, 209; abst. *Jahr. Chem.* 1894, **47**, 440. A. Neuburger, *Zts. ang. Chem.* 1905, **18**, 1843. W. Nylander, *Jahr. Chem.* 1866, **19**, 141. E. Peligot, *Ann.* 1847, **39**, 327. C. Rammelsberg, *Ber.* 1872, **5**, 310. W. Ramsay, J. C. S. 1888, **53**, 621. *Zts. physik. Chem.* 1890, **5**, 221; abst. *Jahr. Chem.* 1890, **43**, 483; J. C. S. 1890, **57**, 590; *Chem. News*, 1894, **70**, 187. W. Ramsay and J. Cundall, J. C. S. 1885, **47**, 187, 672; abst. *Jahr. Chem.* 1885, **38**, 425. Streiff, *Ber.* 1872, **5**, 285; abst. *Jahr. Chem.* 1872, **25**, 191. Thomsen, *Thermochem. Unters.* **2**, 199. T. Thorpe and A. Tutton, J. C. S. 1891, **59**, 1019. O. Witt, *Ber.* 1878, **11**, 756; 1879, **12**, 2188. N. Wittorf, *Zts. anorg. Chem.* 1905, **41**, 85. E. Wourtsel, *Compt. rend.* 1920, **170**, 109; abst. J. C. S. 1920, **118**, ii, 108, 174.
2. D. Helbig, *Atti. R. Acad. Lincei*, 1902, (5), **11**, II, 57; 1903, (5), **12**, I, 166; abst. *Jahr. Chem.* 1902, **55**, 380; 1903, **56**, 376, 381.
3. G. Lunge, *Ber.* 1878, **11**, 1641; abst. *Jahr. Chem.* 1878, **31**, 220.
4. E. Divers, J. C. S. 1899, **75**, 86; abst. *Jahr. Chem.* 1899, **52**, 459.
5. O. Witt, *Ber.* 1878, **11**, 756; 1879, **12**, 2188. W. Ramsay and J. Cundall, J. C. S. 1885, **47**, 187, 672. A. Geuther, *Ann.* 1888, **245**, 961. G. Lunge and G. Porschnew, *Zts. anorg. Chem.* 1894, **7**, 209. H. Dixon and J. Peterkin, J. C. S. 1899, **75**, 614.
6. N. von Wittorf, *Zts. anorg. Chem.* 1904, **41**, 85.

liquid nitric oxide.¹ Nitrogen trioxide apparently exists in an isomeric² or polymetric³ form. A recent patent⁴ describes the preparation of concentrated nitrogen trioxide from dilute nitrous gases, with the simultaneous formation of pure nitrates.

Nitrogen Tetroxide. Nitrogen Dioxide, Nitrogen Peroxide, Hypoazotid, Nitroxin, NO_2 ,⁵ is the red fumes given off when

1. L. Francesconi and H. Sciaeca, *Gaz. chim. ital.* 1904, **34**, i, 447; abst. *Jahr. Chem.* 1904, **57**, 489. M. Berthelot, *Compt. rend.* 1899, **129**, 137. G. Baume and M. Robert, *Compt. rend.* 1919, **169**, 968; abst. *C. A.* 1920, **14**, 701; *J. S. C. I.* 1920, **39**, 61-A.

2. H. and M. Baker, *Chem. News*, 1913, **107**, 5; *J. C. S.* 1907, **91**, 1862; 1912, **101**, 2339; abst. *J. S. C. I.* 1907, **26**, 1276; 1913, **32**, 83. H. Baker and R. Strutt, *Ber.* 1914, **47**, 1049; abst. *J. S. C. I.* 1914, **33**, 548. H. Baker, E. Tiede, R. Strutt and E. Domeke, *Ber.* 1914, **47**, 2283; abst. *J. C. S.* 1914, **106**, ii, 724.

3. B. Jones, *J. C. S.* 1914, **105**, 2310; abst. *J. S. C. I.* 1914, **33**, 1206. See also A. Egerton, *J. C. S.* 1914, **105**, 647. D. Helbig, *Gaz. chim. ital.* 1903, **33**, 454; abst. *Chem. Ztg.* 1903, **27**, 262; *J. S. C. I.* 1903, **22**, 1193. F. Raschig, *Zts. anorg. Chem.* 1913, **84**, 115; *Zts. ang. Chem.* 1905, **18**, 128, 1281; 1907, **20**, 696, 1910. O. Schmidt and R. Böcker, *Ber.* 1906, **39**, 1368. H. LeBlanc, *Zts. Elektrochem.* 1906, **13**, 511. G. Lunge, *Zts. ang. Chem.* 1906, 907; 1907, **20**, 1716. G. Klinger, *Zts. ang. Chem.* 1914, **27**, 7. E. Müller, *Zts. anorg. Chem.* 1912, **76**, 230.

4. C. Schlarb, D. R. P. 243839, 1909; abst. *C. A.* 1912, **6**, 2299; *Chem. Zentr.* 1912, **83**, i, 865; *Chem. Ztg. Rep.* 1912, **36**, 171; *Wag. Jahr.* 1912, **58**, i, 457; *Zts. ang. Chem.* 1912, **25**, 595; D. R. P. 243892, 1909; abst. *C. A.* 1912, **6**, 2299; *Chem. Zentr.* 1912, **83**, i, 866; *Chem. Ztg. Rep.* 1912, **36**, 170; *Wag. Jahr.* 1912, **58**, i, 418; *Zts. ang. Chem.* 1912, **25**, 596; *Zts. Schiess. Spreng.* 1912, **7**, 143. *Aust. P. Ann.* 2427, 1911.

5. L. Bell, *Am. Chem. J.* 1885, **7**, 32; abst. *Jahr. Chem.* 1885, **38**, 324. M. Berthelot, *Compt. rend.* 1878, **77**, 1448; 1880, **90**, 779; 1891, 1343; 1898, **127**, 83; *Bull. Soc. Chim.* 1874, (2), **21**, 53; *Jahr. Chem.* 1874, **27**, 220, 221; 1880, **33**, 118; 1891, **44**, 518. M. Berthelot and J. Ogier, *Compt. rend.* 1882, **94**, 916; abst. *Jahr. Chem.* 1882, **35**, 113. A. Besson, *Compt. rend.* 1889, **108**, 1012; 1896, **123**, 51; abst. *Bull. Soc. Chim.* 1889, (3), **1**, 771. L. Bleckrode, *Wied. Ann.* 1878, **3**, 161; abst. *Jahr. Chem.* 1878, **31**, 148. J. Boguski, *Compt. rend.* 1889, **109**, 804; abst. *Zts. physik. Chem.* 1890, **5**, 69; *Jahr. Chem.* 1889, **42**, 290; 1890, **43**, 316. G. Bruni and P. Berti, *Atti. accad. dei Lincei (Roma)*, 1900, (5), **9**, i, 321; abst. *Gaz. chim. ital.* 1900, **30**, II, 151; *Chem. Centr.* 1900, **71**, II, 80. J. Cundall, *J. C. S.* 1895, **67**, 719; *Chem. News*, 1895, **72**, 56; *Jahr. Chem.* 1895, **48**, 367. H. Deville and L. Troost, *Compt. rend.* 1867, **64**, 237; abst. *Jahr. Chem.* 1867, **20**, 177. E. Divers, *Proc. Chem. Soc.* 1903, **19**, 283; abst. *J. C. S.* 1904, **85**, 110. E. Divers and T. Schimidzu, *J. C. S.* 1885, **47**, 630; *Jahr. Chem.* 1885, **38**, 428. C. Drion, *Ann. Chim. Phys.* 1859, (3), **56**, 5; abst. *Jahr. Chem.* 1859, **12**, 18. C. Duisburg, *Zts. ang. Chem.* 1897, **10**, 492. P. Dulong, *Ann. Chim. Phys.* 1816, **2**, 517; abst. *Gilb. Ann.* 1818, **58**, 53. A. Exner, *Wien. Akad. Ber.* (2 abt.) 1872, **65**, 120; abst. *Jahr. Chem.* 1872, **25**, 191. J. Fritzsche, *J. prakt. Chem.* 1841, **22**, 21. L. Friedburg, *Chem. News*, 1883, **47**, 52; abst. *Jahr. Chem.* 1883, **36**, 307. C. Feliciani, *Phys. Zts.* 1905, **6**, 20; abst. *Chem. Centr.* 1905, **76**, i, 331. P. Frankland and R. Farmer, *J. C. S.* 1901, **79**, 1356; abst. *Chem. Centr.* 1902, **73**, i, 7. P. Fraser and G. Highley, *Am. Chem. J.* 1899, **21**, 377. L. Gay-Lussac, *Ann. Chim. Phys.* 1816, **1**, 394; *Gilb. Ann.* 1818, **58**, 29. A. Geuther, *J. prakt. Chem.* 1873, **116**, 854; abst. *Jahr. Chem.* 1873, **26**, 236. *Ann.* 1888, **245**, 96. A. Geuther and A. Michaelis, *Ber.* 1871, **4**, 766. C.

nitric oxide comes in contact with oxygen or air, or by gently heating a mixture of nitric and sulfuric acids of definite concentrations;¹ also by mixing the fumes from nitric acid and arsenious

- Girard and A. Pabst. *Bull. Soc. Chim.* 1878, (2), **30**, 531; abst. *Jahr. Chem.* 1878, **31**, 223. J. Gladstone, *Chem. News*, 1887, **55**, 390. D. Gernez, *Compt. rend.* 1872, **74**, 465; abst. *Jahr. Chem.* 1872, **25**, 137. R. Günsberg, *Wien. Akad. Ber.* 1873, **68**, 498. A. Guntz, *Bull. Soc. Chim.* 1892, (3), **7**, 275; abst. *Jahr. Chem.* 1892, **45**, 745. C. Hasenbach, *J. prakt. Chem.* 1871, **112**, 1; abst. *Jahr. Chem.* 1871, **24**, 237. S. Hasselberg, *Zts. anal. Chem.* 1879, **18**, 571. D. Helbig, *Atti. Accad. dei Lincei*, 1902, (5), **11**, II, 311; 1903, (5), **12**, I, 211. L. Henry, *Bull. de l'Acad. R. de Belg.* 1874, (2), **38**, 1; abst. *Jahr. Chem.* 1876, **29**, 219. K. Heumann, *Anl. zum Exper.* 1893, 178. F. Kuhlmann, *Ann.* 1839, **29**, 272; 1841, **39**, 319. A. Kundt, *Pogg. Ann.* 1870, **141**, 157; *Arch. ph. Nat.* **39**, 258; *Jahr. Chem.* 1870, **23**, 172. E. Luck, *Zts. anal. Chem.* 1869, **8**, 402; abst. *Zts. Chem.* 1870, **13**, 287. Zts. anal. Chem. 1874, **13**, 255. G. Lunge, *Ber.* 1878, **11**, 1229; 1882, **15**, 488. G. Lunge and E. Weintraub, *Zts. ang. Chem.* 1899, **39**, 417. J. Sudborough and J. Millar, *J. C. S.* 1891, **59**, 270; abst. *Jahr. Chem.* 1891, **44**, 427. G. Magnanin and G. Malaginini, *Atti. Accad. dei Lincei*, 1897, (5), **6**, II, 22; abst. *Chem. Centr.* 1897, **68**, II, 460. V. Meyers, *Ann.* 1874, **171**, 5. R. Müller, *Ann.* 1862, **122**, 1. A. Nadejdin, *Gaz. chim. ital.* 1884, **14**, 548; *Ann. Phys. Beibl.* 1885, **9**, 721; abst. *Jahr. Chem.* 1885, **38**, 158. E. and L. Natanson, *Wied. Ann.* 1885, **24**, 454; 1886, **27**, 606. A. Naumann, *Ann. Suppl.* 1868, **6**, 203. W. Nernst, *Boltzmann Festschrift*, 1904, 904. S. and A. Neumann, *Ber.* 1878, **11**, 2045. W. Nylander, *Zts. Chem.* 1866, **9**, 66; abst. *Jahr. Chem.* 1866, **19**, 141. J. Ogier, *Analyse des gaz.* 86. W. Ostwald, *J. C. S.* 1892, **61**, 242; abst. *Jahr. Chem.* 1892, **45**, 389. O. Piloty and B. Schwerin, *Ber.* 1901, **34**, 1884. E. Peligot, *Ann. Chim. Phys.* 1833, **54**, 17; 1835, **58**, 87; *Ann.* 1834, **9**, 259; 1841, **39**, 327. C. Hasenbach, *J. prakt. Chem.* 1871, **112**, 1. L. Playfair and J. Wanklyn, *J. C. S.* 1862, **15**, 142; *Ann.* 1862, **122**, 245. A. Richardson, *J. C. S.* 1887, **51**, 397; abst. *Jahr. Chem.* 1887, **40**, 403. W. Ramsay, *J. C. S.* 1888, **53**, 621; 1890, **57**, 590; *Zts. physik. Chem.* 1889, **3**, 66; 1890, **5**, 221; *Chem. News*, 1890, **61**, 91; *Jahr. Chem.* 1888, **41**, 117; 1889, 407. W. Ramsay and J. Cundall, *J. C. S.* 1885, **47**, 672. G. Salet, *Compt. rend.* 1868, **67**, 488. A. Semenov, *Zts. Chem.* 1864, **7**, 129; abst. *Jahr. Chem.* 1864, **17**, 480. C. Schönbein, *Pogg. Ann.* 1848, **73**, 326; abst. *Jahr. Chem.* 1847-1848, **1**, 333. *J. prakt. Chem.* 1852, **55**, 146. P. Sabatier and J. Senderens, *Compt. rend.* 1892, **115**, 236; *Ann. Chim. Phys.* 1896, (7), **7**, 348; abst. *Jahr. Chem.* 1892, **45**, 594; 1896, **49**, 411. J. Thomsen, *Ber.* 1872, **5**, 508. D. Tommasi, *Bull. Soc. Chim.* 1872, (2), **17**, 396; *Compt. rend.* 1872, **74**, 987. E. Turpin, *Ber.* 1882, **15**, 2946. E. Tassell, *Compt. rend.* 1890, **110**, 1264; abst. *Jahr. Chem.* 1890, **42**, 500. T. Thorpe, *Jahr. Chem.* 1880, **23**, 19. T. Thorpe and A. Tutton, *J. C. S.* 1891, **59**, 1019. L. Troost, *Compt. rend.* 1878, **86**, 331, 1394; abst. *Jahr. Chem.* 1878, **31**, 34. V. Thomas, *Compt. rend.* 1895, **120**, 1115; 1896, **122**, 1060; 1896, **123**, 51; *Bull. Soc. Chim.* 1895, (3), **13**, 722; 1896, **15**, 1090; *Ann. Chim. Phys.* 1898, (7), **13**, 145; abst. *Jahr. Chem.* 1895, **48**, 634; 1896, **49**, 408; 1897, **50**, 630; 1898, **51**, 257. L. Vanino, *Ber.* 1899, **32**, 1392. W. Vaubel, *J. prakt. Chem.* 1897, **163**, 542. R. Weber, *Pogg. Ann.* 1867, **130**, 277. C. Weltzien, *Ann.* 1860, **115**, 219. C. Winkler, *Zts. Chem.* 1869, **12**, 715; abst. *Jahr. Chem.* 1869, **22**, 207. O. Witt, *Tagebl. d. Naturforschervers. zu Baden-Baden*, 1894, 194. E. Wourtsel, *Compt. rend.* 1919, **169**, 1397; abst. *C. A.* 1920, **14**, 667; *J. S. C. I.* 1920, **39**, 154-A.
1. J. Cundall, *J. C. S.* 1891, **59**, 1076; abst. *Bull. Soc. Chim.* 1896, **16**, 826; *Ber.* 1892, **25**, 492-R.

oxide with oxygen.¹ In a process patented in England,² NO₂ is extracted from air mixtures containing small quantities of NO by striking an electric arc in the air. The Badische Anilin und Soda Fabrik³ remove from nitric oxide any NO₂ present, dry the remaining NO and convert this to NO₂ by means of dry O. The process of the Allgemeine Elektrizitäts Ges.⁴ for obtaining NO₂ from mixtures of NO and air consists in subjecting the gaseous mixture at a low temperature to a powerful centrifugal action for the purpose of withdrawing the mist of NO₂ produced from the gaseous mixture by means of the cooling action.

Bergius obtains concentrated nitric acid from mixtures of gaseous NO₂ with gases containing oxygen and water, by causing

1. P. Frankland and R. Farmer, J. C. S. 1901, **79**, 1356. J. Cohen and H. Calvert, J. C. S. 1897, **71**, 1052. W. Argo, J. physik. Chem. 1914, **18**, 438; abst. J. S. C. I. 1914, **33**, 592. For NO₂ explosives, see H. Kast and P. Günther, Zts. Schiess. Spreng. 1919, **14**, 81, 103; abst. Chem. Zentr. 1919, **90**, II, 794; J. S. C. I. 1919, **38**, 603-A. For manufacture of liquid NO₂, refer to W. Bousfield and Nobel's Explosives Co., E. P. 131642, 1918; abst. J. S. C. I. 1919, **38**, 763-A. Norske Hydro-Elektrisk Kvaedstofaktieselskab, Norw. P. 2729, 1918. E. P. 124191, 1918, abst. C. A. 1919, **13**, 1623.

2. Allgemeine Elektrizitäts Ges., E. P. 9233, 1908; abst. J. S. C. I. 1908, **27**, 940. For the constitution of N₂O₄, see G. Oddo, Gaz. chim. ital. 1915, **45**, I, 413; abst. J. S. C. I. 1915, **34**, 797.

3. Badische Anilin und Soda Fabrik., D. R. P. 231805; abst. Chem. Zentr. 1911, **82**, I, 852; Chem. Ztg. Rep. 1911, **35**, 127; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 565. D. R. P. 242288, 1908; abst. C. A. 1910, **4**, 2153; Chem. Zentr. 1912, **83**, I, 296; Chem. Ztg. Rep. 1912, **36**, 43; Wag. Jahr. 1912, **58**, I, 415; Zts. ang. Chem. 1912, **25**, 328; Zts. Schiess. Spreng. 1912, **7**, 185. The density of nitrogen tetroxide has been given by Kaye and Laby at 760 mm. as: 38.37 at 26.7°; 35.82 at 39.8°; 30.12 at 60.2°; 26.06 at 80.6°; 24.33 at 100.1°; 23.46 at 121.5°; 22.88 at 154°, and 22.73 at 183.2°, from which it appears that while at lower ranges the gas is almost completely N₂O₄, at temperatures above 140°, it is practically entirely dissociated. See F. Gros and Bouchardy, E. P. 131336, 1918; abst. J. S. C. I. 1919, **38**, 763-A.

4. E. P. 9233, 1908; abst. J. S. C. I. 1908, **27**, 940; E. P. 10479, 1912; abst. J. S. C. I. 1912, **31**, 1032; C. A. 1913, **7**, 3644. F. P. 388281, 1908; abst. J. S. C. I. 1908, **27**, 897; Mon. Sci. 1909, **71**, 110; Chem. Ztg. Rep. 1908, **32**, 452. D. R. P. 199561, 1907; abst. J. S. C. I. 1908, **27**, 856; Mon. Sci. 1911, **75**, 51; Chem. Zentr. 1908, **79**, II, 272; Chem. Ztg. Rep. 1908, **32**, 389; Chem. Zts. 1908, **7**, 889; Jahr. Chem. 1905-1908, I, 1785; Wag. Jahr. 1908, **54**, I, 423; Zts. ang. Chem. 1908, **21**, 1851; Zts. Schiess. Spreng. 1908, **3**, 334. F. P. 389112, 1908; abst. J. S. C. I. 1908, **27**, 986; Mon. Sci. 1911, **75**, 572. F. P. 411693, abst. C. A. 1912, **6**, 1884; Mon. Sci. 1913, **79**, 75; Chem. Ztg. Rep. 1910, **34**, 425. F. P. 441706, 1912; abst. J. S. C. I. 1912, **31**, 922. U. S. P. 1070070, 1913; abst. J. S. C. I. 1913, **32**, 911; C. A. 1913, **7**, 3278. F. P. 426307, 1911; abst. J. S. C. I. 1911, **30**, 1012; Mon. Sci. 1913, **79**, 122. E. P. 5282, 1911; abst. J. S. C. I. 1912, **31**, 231. F. P. 426307; abst. J. S. C. I. 1911, **30**, 1012. Aust. P. 52690; Swiss P. 43628. A. Bogrodski, J. Russ. Chem. Phys. Soc. 1905, **37**, 703; abst. Chem. Centr. 1905, **76**, II, 954. G. Lunge and E. Berl, Zts. ang. Chem. 1906, **19**, 807. Besson and Rosset, Compt. rend. 1906, **142**, 633; abst. Chem. Centr. 1906, **77**, I, 1319. F. Raschig, Zts. ang. Chem. 1905, **18**, 1281; abst. Chem. Centr. 1905, **76**, II, 932.

the reaction to take place at higher temperatures and at high pressures which prevents the decomposition.¹ The process of K. von Vossinghoff-Scheel² is similar.³ F. Raschig⁴ obtained an isomeric nitrogen tetroxide, called by him "isonitrogen tetroxide" as blue crystals by the action of air at low temperatures upon nitric oxide.

Liquid NO₂ has a sp. gr. of 1.49 at 0°, boiling at 22°, forming a reddish brown vapor of an unpleasant and penetrating odor. The density of the vapor is 2.52 at 24.5° (air = 1),⁵ the composition of the gas at 100° being 79.23% NO₂ and 20.77% N₂O₄.⁶ When diluted with chloroform a similar dissociation is under gone.⁷

Liquid or solid nitrogen tetroxide acts as a solvent for many substances as iodine, bromine and numerous organic compounds,⁸ while on the other hand, carbon tetrachloride, chloroform, pentachlorethane,⁹ ethyl bromide, chlor-, brom-, and iodo-benzene¹⁰

1. D. R. P. Ann. B. 53617.
2. D. R. P. 225706, 1908; abst. J. S. C. I. 1910, **29**, 1377; Mon. Sci. 1914, **81**, 87; Chym. Zentr. 1910, **81**, II, 1007; Chem. Ztg. Rep. 1910, **34**, 498; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 473; Zts. ang. Chem. 1910, **23**, 2189; Zts. Schiess. Spreng. 1910, **5**, 359.
3. I. Moscicki, D. R. P. 244259; abst. C. A. 1912, **6**, 1825; Chem. Zentr. 1911, **82**, I, 1618; Chem. Ztg. Rep. 1911, **35**, 302; Wag. Jahr. 1911, **57**, I, 652; Zts. ang. Chem. 1911, **24**, 1097. F. P. 3583, 14259, 1906; 21959, 1908; abst. J. S. C. I. 1907, **26**, 261, 876; 1909, **28**, 529. F. P. 369387; abst. Mon. Sci. 1908, **69**, 76; 1911, **75**, 571. F. P. 380614, 395424; abst. Mon. Sci. 1911, **75**, 571, 572. U. S. P. 920610, 933094; abst. Chem. Ztg. Rep. 1909, **33**, 311, 542. Belg. P. 201874, abst. J. S. C. I. 1907, **26**, 157, 876; 1908, **27**, 22; 1909, **28**, 529. Swiss P. 33694, 1905; abst. Zts. ang. Chem. 1906, **19**, 980; Zts. Elektrochem. 1906, **13**, 241. Maschinenfabrik Buckau, D. R. P. 234509; abst. C. A. 1912, **6**, 1867; Chem. Ztg. Rep. 1911, **35**, 346; Wag. Jahr. 1911, **57**, I, 653; Zts. ang. Chem. 1911, **24**, 1098. See also in this connection, A. Mandl and F. Russ, Zts. ang. Chem. 1908, **21**, 486, 2131. F. Foerster and M. Koch, Zts. ang. Chem. 1908, **21**, 2161.
4. Zts. ang. Chem. 1907, **20**, 694, 709, 890, 1809; abst. C. A. 1907, **1**, 1896, 1899; 1908, **2**, 307; J. C. S. 1907, **92**, ii, 455; 1908, **94**, ii, 30; Chem. Zentr. 1907, **78**, II, 490; 1908, **79**, I, 201.
5. L. Playfair and J. Wanklyn, Proc. Roy. Soc. Edin. **4**, 395; Trans. Roy. Soc. Edin. **22**, III, 441; abst. Chem. News, 1861, **3**, 122; Phil. Mag. 1861, (4), **21**, 398; Rep. Chim Pure, 1862, **4**, 209, 241; Ann. 1862, **121**, 101, **122**, 245. Jahr. Chem. 1861, **14**, 22; Zts. Chem. 1861, **4**, 231, 370; J. C. S. 1862, **15**, 142.
6. H. Deville and L. Troost, Compt. rend. 1867, **64**, 237.
7. J. Cundall, J. C. S. 1891, **59**, 1076; 1895, **67**, 794.
8. G. Bruni and P. Berth, Gaz. chim. ital. 1900, **30**, ii, 151; abst. Chem. Centr. 1900, **71**, II, 80, 757. P. Frankland and R. Farmer, J. C. S. 1901, **79**, E356.
9. Soc. Anon. LeNitrogene, E. P. 1143, 1911; abst. Chem. Ztg. Rep. 1912, **36**, 371.
10. P. Guye, F. P. 404630; abst. Mon. Sci. 1910, **73**, 170.

have been used as solvents for nitrogen tetroxide in processes for separating this from gaseous mixtures by cooling. NO_2 has been used for bleaching flour,¹ for separating iodine and bromine from mother liquors,² and in the manufacture of explosives by heating lead nitrate.³ L. Doyen⁴ colors wood for musical instruments, furniture, etc., by treatment in a closed chamber with nitrogen peroxide vapors. In many reactions NO_2 acts as a true peroxide.⁵

Nitrogen Pentoxide.⁶ Nitric anhydride, N_2O_5 , was discovered in 1849 by H. Deville,⁷ and may be conveniently prepared by withdrawing the element of water from perfectly pure anhydrous nitric acid; by the action of ozone on NO_2 ;⁸ by the electric oxidation of solutions of NO_2 in HNO_3 ;⁹ by the fractionation of a mixture of strong nitric acid and P_2O_5 ;¹⁰ by electrolytically oxidizing a solution of NO_2 in nitrous or nitric acid.¹¹ When prepared by

1. Scherings, Chem. Weekblad, **12**, 46. Steensma, Chem. Weekblad, **12**, 46.

2. J. Pellicieux and A. Mazé-Launay, E. P. 3448, 1871.

3. E. Turpin, E. P. 4544, 1881. A. Richardson, J. C. S. 1887, **51**, 397.

4. E. P. 1063, 1913; abst. C. A. 1914, **8**, 2497; J. S. C. I. 1913, **32**, 912; Chem. Ztg. Rep. 1914, **38**, 395.

5. E. Divers, J. C. S. 1904, **85**, 110. For carrying liquid nitrogen peroxide on cylindrical railway trucks, see Zts. Schiess. Spreng. 1914, **9**, 326.

6. For general data on nitrogen pentoxide, refer to M. Berthelot, Bull. Soc. Chim. 1874, (2), **21**, 53; Compt. rend. 1874, **78**, 99, 162, 205, 1173; 1880, **90**, 779; Ann. Chim. Phys. 1875, (5), **6**, 145; Jahr. Chem. 1874, **27**, 113, 220; 1875, **28**, 74; 1880, **33**, 117. J. Dumas, Compt. rend. 1849, **28**, 323; Jahr. Chem. 1849, **3**, 257. J. Giersbach and A. Kessler, Zts. physik. Chem. 1888, **2**, 676. D. Helbig, Atti Accad. dei Lincei (Roma), 1902, (5), **11**, II, 311; 1903, **12**, I, 211. Odet and Vignon, Compt. rend. 1869, **69**, 11, 1142; 1870, **70**, 96; Ber. 1869, **2**, 714; J. prakt. Chem. 1869, **108**, 313. Thomsen, Thermochem. Unterss. 1884, **2**, 199. V. Veley and J. Manley, Chem. Ztg. 1905, **29**, 1207. R. Weber, J. prakt. Chem. 1872, (2), **6**, 342; Pogg. Ann. 1872, **147**, 113; Ber. 1872, **5**, 454; Jahr. Chem. 1872, **25**, 194.

7. Ann. Chim. Phys. 1850, **28**, 241; Jahr. Chem. 1849, **3**, 256; J. prakt. Chem. 1849, **47**, 185; 1850, **49**, 407. See also G. Lunge, Ber. 1881, **14**, 2196.

8. W. Smith, J. S. C. I. 1892, **11**, 867; 1893, **12**, 10.

9. A. Lidoff, J. Russ. Phys. Chem. Soc. 1903, **35**, 59. Salpetersäure Industrie Ges., D. R. P. 231546, abst. Mon. Sci. 1915, **82**, 56; Chem. Zentr. 1911, **82**, I, 767; Chem. Ztg. Rep. 1911, **35**, 111; Chem. Zts. 1911, **10**, No. 2501; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 565; Zts. Schiess. Spreng. 1911, **6**, 157. E. P. 9884, 22319, 1910; abst. J. S. C. I. 1910, **29**, 1157; 1911, **30**, 685. E. P. 131334, abst. J. S. C. I. 1919, **38**, 763-A.

10. P. Villard, Compt. rend. 1894, **118**, 1096. F. Russ and E. Pokorny, Monatsh. 1913, **34**, 1051; abst. Chem. Centr. 1913, **84**, II, 1271; J. S. C. I. 1913, **32**, 825. For nitrogen hexoxide, see F. Raschig, Chem. Ztg. 1911, **35**, 1906; abst. J. S. C. I. 1911, **30**, 1208. P. Gros and Bouchardy, E. P. 131334, 1918; abst. C. A. 1920, **14**, 103.

11. Elektrochemische Werke Ges., E. P. 15432, 1911; abst. C. A. 1913, **7**, 27; J. S. C. I. 1911, **30**, 1251. Aust. P. 52690, 1911. F. Russ and L. Ehrlich, E. P. 443620, 1912; abst. J. S. C. I. 1912, **31**, 1031; C. A. 1913, **7**, 1142; Mon. Sci. 1913, **79**, 142; Chem. Ztg. Rep. 1913, **37**, 33. See I. Mo-

one of the methods indicated above, nitrogen pentoxide is a colorless solid, readily melting with the evolution of dark fumes. It is a powerful and difficultly controllable oxidizer. With sulfur it forms nitrosulfonic anhydride. When brought in contact with HNO_3 , the anhydride combines to form the compound $\text{N}_2\text{O}_5 \cdot 2\text{HNO}_3$.

Manufacture of Nitric Acid with Chili Saltpeter.¹ This

cicki, E. P. 27006, 1906; abst. J. S. C. I. 1908, **27**, 22; F. P. 380614, 1906; abst. J. S. C. I. 1908, **27**, 22; Mon. Sci. 1911, **75**, 571, 572. F. Bayer & Co., Belg. P. 172250, 1903. Elektrochemische Werke Ges., Belg. P. 207237, 207403, 207516, 1908; 236562, 1911; Swiss P. 43628, 43629, 43778, 1908; 51812, 1910; 57534, 1911; abst. C. A. 1913, **7**, 3002. Can. P. 142471, 1912.

1. D. R. P. 39659; abst. Wag. Jahr. 1887, **33**, 560. D. R. P. 46096; abst. Ber. 1889, **22**, 152; Chem. Centr. 1889, **60**, 1, 688; Jahr. Chem. 1889, **42**, 2651; Wag. Jahr. 1889, **35**, 456. D. R. P. 46724; abst. Ber. 1889, **22**, 304; Wag. Jahr. 1889, **35**, 456. D. R. P. 59099; abst. Ber. 1892, **25**, 223; Wag. Jahr. 1891, **37**, 392; Zts. ang. Chem. 1891, **4**, 609. D. R. P. 63207; abst. Mon. Sci. 1896, **48**, 108; 1902, **58**, 24; Ber. 1892, **25**, 878; Chem. Zts. 1902, **1**, 14; Jahr. Chem. 1892, **45**, 2695; 1894, **47**, 2297; Wag. Jahr. 1892, **38**, 357; Zts. ang. Chem. 1892, **5**, 526. D. R. P. 63714, 63799; abst. Ber. 1892, **25**, 878; Chem. Zts. 1902, **1**, 14; Wag. Jahr. 1892, **38**, 355; Zts. ang. Chem. 1892, **5**, 552. D. R. P. 73421; abst. Ber. 1894, **27**, 429; Chem. Zts. 1902, **1**, 14; Wag. Jahr. 1894, **40**, 493; Zts. ang. Chem. 1894, **7**, 174. D. R. P. 79645; abst. Ber. 1895, **28**, 482; Jahr. Chem. 1895, **48**, 569; Wag. Jahr. 1895, **41**, 450; Zts. ang. Chem. 1895, **8**, 170. D. R. P. 82573; abst. Mon. Sci. 1896, **48**, 72; 1902, **58**, 23; Ber. 1895, **28**, 876; Chem. Centr. 1895, **66**, 11, 1024; Jahr. Chem. 1895, **48**, 570; Wag. Jahr. 1895, **41**, 449; Zts. ang. Chem. 1895, **8**, 570. D. R. P. 83097; abst. Ber. 1895, **28**, 1031; Chem. Centr. 1896, **67**, 1, 80; Chem. Ztg. 1895, **19**, 2127; Jahr. Chem. 1895, **48**, 717; Wag. Jahr. 1895, **41**, 327; Zts. ang. Chem. 1895, **8**, 626. D. R. P. 85040, 85242; abst. Mon. Sci. 1896, **48**, 501; 1897, **50**, 65; Ber. 1896, **29**, 318; Chem. Centr. 1896, **67**, 1, 1287; Chem. Ztg. 1896, **20**, 221; Jahr. Chem. 1896, **49**, 1323; Wag. Jahr. 1895, **41**, 614; Zts. ang. Chem. 1896, **9**, 175. D. R. P. 87982; abst. Ber. 1896, **29**, 807; Chem. Ztg. 1896, **20**, 768; Wag. Jahr. 1896, **42**, 409; Zts. ang. Chem. 1896, **9**, 573. D. R. P. 88321; abst. Ber. 1896, **29**, 884; Chem. Ztg. 1896, **20**, 825; Wag. Jahr. 1896, **42**, 406; Zts. ang. Chem. 1896, **9**, 632. D. R. P. 99531; abst. Mon. Sci. 1899, **54**, 51; Chem. Centr. 1899, **70**, 1, 79; Chem. Ztg. 1898, **22**, 977; Jahr. Chem. 1898, **51**, 765; Wag. Jahr. 1898, **44**, 416; Zts. ang. Chem. 1898, **11**, 1057. D. R. P. 104357; abst. Mon. Sci. 1900, **56**, 13; Chem. Centr. 1899, **70**, 11, 800; Chem. Ztg. 1899, **23**, 773; Jahr. Chem. 1899, **52**, 471; Wag. Jahr. 1899, **45**, 409; Zts. ang. Chem. 1899, **12**, 907. D. R. P. 105704; abst. Mon. Sci. 1900, **56**, 116; Chem. Centr. 1900, **71**, 1, 79; Chem. Ztg. 1899, **23**, 1030; Jahr. Chem. 1899, **52**, 471; Wag. Jahr. 1899, **45**, 409; Zts. ang. Chem. 1899, **12**, 1063. D. R. P. 106962; abst. Mon. Sci. 1900, **56**, 117; Chem. Centr. 1900, **71**, 1, 636; Chem. Ztg. 1900, **24**, 80; Chem. Zts. 1902, **1**, 14; Jahr. Chem. 1900, **53**, 239; Wag. Jahr. 1899, **45**, 407; Zts. ang. Chem. 1899, **12**, 1138. D. R. P. 110254; abst. Mon. Sci. 1900, **56**, 185; Chem. Centr. 1900, **71**, 11, 228; Chem. Ztg. 1900, **24**, 316; Jahr. Chem. 1900, **53**, 240; Wag. Jahr. 1900, **46**, 1, 393; Zts. ang. Chem. 1900, **13**, 373; abst. Mon. Sci. 1902, **58**, 152; Chem. Centr. 1902, **73**, 1, 286; Chem. Ztg. 1902, **26**, 73; Chem. Zts. 1902, **1**, 475; Jahr. Chem. 1902, **55**, 383; Wag. Jahr. 1902, **48**, 1, 359. D. R. P. 136679; abst. Chem. Ztg. 1903, **27**, 57; Chem. Zts. 1903, **2**, 530; Wag. Jahr. 1902, **48**, 1, 360. D. R. P. 136789, 144638, 155006; abst. Mon. Sci. 1905, **63**, 51; Chem. Centr. 1904, **74**, 11, 1267; Chem. Ztg. 1904,

process, until comparatively recently, was practically the only method for the commercial manufacture of nitric acid, and involves the heating of commercial sodium nitrate with sulfuric acid. 28, 1001; Chem. Zts. 1905, 4, 123; Jahr. Chem. 1904, 57, 490; Wag. Jahr. 1904, 50, I, 338; Zts. ang. Chem. 1905, 18, 105. D. R. P. 155095; abst. Mon. Sci. 1905, 63, 51; Chem. Centr. 1904, 74, II, 1268; Chem. Ztg. 1904, 28, 1028; Chem. Zts. 1905, 4, 123; Jahr. Chem. 1904, 57, 490; Wag. Jahr. 1904, 50, I, 337; Zts. ang. Chem. 1905, 18, 105. D. R. P. 170352; abst. Mon. Sci. 1907, 67, 145; Chem. Centr. 1906, 76, II, 185; Chem. Ztg. 1906, 30, 562; Chem. Zts. 1907, 6, 19; Jahr. Chem. 1905-1908, I, 1793; Wag. Jahr. 1906, 52, I, 445; Zts. ang. Chem. 1907, 20, 972; Zts. Schiess. Spreng. 1906, 1, 180. D. R. P. 180052; abst. Mon. Sci. 1909, 71, 74; Chem. Zentr. 1907, 77, I, 1083; Chem. Ztg. Rep. 1907, 31, 86; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1906, 52, I, 446; Zts. ang. Chem. 1907, 20, 1329; Zts. Schiess. Spreng. 1907, 2, 35. D. R. P. 189865; abst. Mon. Sci. 1910, 73, 66; Chem. Zentr. 1907, 78, II, 1954; Chem. Zts. 1907, 6, No. 389; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1907, 53, I, 409; Zts. ang. Chem. 1908, 21, 798; Zts. Schiess. Spreng. 1907, 2, 410. D. R. P. 191912; abst. Mon. Sci. 1910, 73, 67; Chem. Zentr. 1908, 79, I, 315; Chem. Ztg. Rep. 1907, 31, 633; Chem. Zts. 1908, 7, 490; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1907, 53, I, 410; Zts. ang. Chem. 1908, 21, 798; Zts. Schiess. Spreng. 1907, 2, 455. D. R. P. 202560, 1907; abst. J. S. C. I. 1909, 28, 90; Mon. Sci. 1911, 75, 123; Chem. Zentr. 1908, 79, II, 1549; Chem. Ztg. Rep. 1908, 32, 572; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1908, 54, I, 425; Zts. ang. Chem. 1908, 21, 2518; Zts. Schiess. Spreng. 1908, 3, 416. D. R. P. 208143; abst. Mon. Sci. 1912, 77, 82; 1913, 79, 65; Chem. Zentr. 1909, 80, I, 1279; Chem. Ztg. Rep. 1909, 33, 186; Chem. Zts. 1909, 8, No. 1398; Jahr. Chem. 1909, 62, I, 535; 1910, 63, I, 586; Wag. Jahr. 1909, 55, I, 424; Zts. ang. Chem. 1909, 22, 748; Zts. Schiess. Spreng. 1909, 4, 215. D. R. P. 210803; abst. Mon. Sci. 1912, 77, 99; Chem. Zentr. 1909, 80, II, 159; Chem. Ztg. Rep. 1909, 33, 339; Chem. Zts. 1910, 9, No. 1565; Jahr. Chem. 1909, 62, 536; Wag. Jahr. 1909, 55, I, 418; Zts. ang. Chem. 1909, 22, 1468; Zts. Schiess. Spreng. 1909, 4, 291. D. R. P. 227377; abst. Mon. Sci. 1914, 81, 85; Chem. Zentr. 1910, 81, II, 1419; Chem. Ztg. Rep. 1910, 34, 561; Chem. Zts. 1911, 10, No. 2363; Jahr. Chem. 1910, 63, I, 586; Wag. Jahr. 1910, 56, I, 482; Zts. ang. Chem. 1910, 23, 2338; Zts. Schiess. Spreng. 1912, 7, 36. D. R. P. 229096, 1908; abst. J. S. C. I. 1911, 30, 84; Mon. Sci. 1914, 81, 86; Chem. Zentr. 82, I, 177; Chem. Ztg. Rep. 1910, 34, 632; Chem. Zts. 1911, 10, No. 2260; Wag. Jahr. 1911, 57, I, 466; Zts. ang. Chem. 1910, 23, 87; Zts. Schiess. Spreng. 1910, 5, 481. D. R. P. 233031; abst. Chem. Zentr. 1911, 82, I, 1261; Chem. Ztg. Rep. 1911, 35, 229; Wag. Jahr. 1911, 57, I, 468; Zts. ang. Chem. 1911, 24, 856; Zts. Schiess. Spreng. 1911, 6, 156. D. R. P. 236341; abst. Chem. Zentr. 1911, 82, II, 314; Chem. Ztg. Rep. 1911, 35, 392; Wag. Jahr. 1911, 57, I, 469; Zts. ang. Chem. 1911, 24, 1580. D. R. P. 237684; abst. C. A. 1912, 6, 1508; Chem. Zentr. 1911, 82, II, 812; Chem. Ztg. Rep. 1911, 35, 464; Wag. Jahr. 1911, 57, I, 472; Zts. ang. Chem. 1911, 24, 1882; Zts. Schiess. Spreng. 1911, 6, 411. D. R. P. 238370; abst. C. A. 1912, 6, 1663; Chem. Zentr. 1911, 82, II, 1078; Chem. Ztg. Rep. 1911, 35, 503; Wag. Jahr. 1911, 57, I, 470; Zts. ang. Chem. 1911, 24, 2029; Zts. Schiess. Spreng. 1911, 6, 411. D. R. P. 241711; abst. C. A. 1912, 6, 2152; Chem. Zentr. 1912, 83, I, 172; Chem. Ztg. Rep. 1912, 36, 8; Wag. Jahr. 1911, 57, I, 469; Zts. ang. Chem. 1912, 25, 136; Zts. Schiess. Spreng. 1912, 7, 78. D. R. P. 252374; abst. C. A. 1913, 7, 863; Chem. Zentr. 1912, 83, II, 1707; Chem. Ztg. Rep. 1912, 36, 663; Wag. Jahr. 1912, 58, I, 421; Zts. ang. Chem. 1912, 25, 2377; Zts. Schiess. Spreng. 1912, 7, 454. D. R. P. 257809; abst. C. A. 1913, 7, 2458; Chem. Zentr. 1913, 84, I, 1245; Chem. Ztg. Rep. 1913, 37, 166; Wag. Jahr. 1913, 59, I, 434; Zts. ang. Chem. 1913, 26, 235; Zts. Schiess. Spreng.

acid, acid sodium sulfate being obtained in addition to the nitric acid. The details of the process will be treated herein in the following rotation of topics:

- (a) Chili Saltpeter.
- (b) Layout and Arrangement of the Nitric Acid Plant.
- (c) Drying the Sodium Nitrate.
- (d) Loading the Nitric Acid Retort.
- (e) Generation of the Nitric Acid.
- (f) Condensation of the Gaseous Nitric Acid.
- (g) Fuel Requirements.
- (h) Yields of Nitric Acid.
- (i) Niter Cake. Commercial Utilization.
- (j) Valentiner Vacuum and Other Processes Employing Sodium Nitrate.
- (k) The Griesheim Nitric Acid Plant.
- (l) Continuous Manufacture of Nitric Acid.

It is computed¹ that the production of nitric acid (calculated as 100% HNO_3) in the United States from sodium nitrate has increased from 89000 tons in 1914, to 650000 tons in 1918. The erection of many new nitric acid plants has provided opportunity for improvements to be made. The installation of modern fire-boxes in place of Dutch ovens under the retorts has effected a reduction in coal consumption of 25%. Acid-proof iron has

1913, **8**, 178. D. R. P. 261634; abst. C. A. 1913, **7**, 3397; Chem. Zentr. 1913, **84**, II, 323; Chem. Ztg. Rep. 1913, **37**, 420; Wag. Jahr. 1913, **59**, I, 435; Zts. ang. Chem. 1913, **26**, 477. D. R. P. 263652; abst. C. A. 1913, **7**, 3929; Chem. Zentr. 1913, **84**, II, 1090; Chem. Ztg. Rep. 1913, **37**, 528; Wag. Jahr. 1913, **59**, I, 430; Zts. ang. Chem. 1913, **26**, 594. D. R. P. 267869; abst. C. A. 1914, **8**, 998; Chem. Zentr. 1914, **85**, I, 197; Chem. Ztg. Rep. 1913, **37**, 695; Wag. Jahr. 1913, **59**, I, 435; Zts. ang. Chem. 1914, **27**, 49. Compare also I. Baggs and W. Simpson, E. P. 956, 1863. P. Ribeau, E. P. 396290. P. de Fontainemoreau, E. P. 13113, 1850. D. Fitz-Gerald and B. Molloy, E. P. 1376, 1872. W. Fuller, E. P. 2673, 1881. C. Rjider, E. P. 9635, 1904; abst. J. S. C. I. 1906, **24**, 123. Anon. Ind. chimique, 1919, **6**, 266; abst. C. A. 1920, **14**, 1187. Agricultural Research Corporation Can. P. 162565, 163922, 1915. H. Akers, Can. P. 151959, 1913. American Cyanamid Co., Can. P. 161112, 161113, 161566, 1915. O. Carlson, Can. P. 156396, 1914. J. Currie, Can. P. 174360, 1917. E. duPont de Nemours Co., Can. P. 167587, 1916. Meister, Lucius & Brining, Can. P. 156378, 1914. T. Fuyiyama, Can. P. 162512, 1915. Haslip & Peacock, Inc., Can. P. 187050. C. Houseman, Chem. Age, 1920, **2**, 198. Nitrogen Products Co., Can. P. 156382, 1914; 162023, 1915; 169161, 169162, 169163, 1916. F. Schmitz, Can. P. 156341, 1913. V. Thrane, Can. P. 181105, 1917. A. White, Chem. Met. Eng. 1920, **22**, 369.

1. E. Franke, J. Ind. Eng. Chem. 1918, **10**, 830; abst. C. A. 1918, **12**, 2412; J. S. C. I. 1918, **37**, 653-A.

been largely used to replace chemical stoneware, and a larger absorption tower capacity has been provided. The average charge of nitrate has been increased 50%. These improvements, together with modifications in the method of operation, have effected an increase in the amount of nitrogen recovered as acid from about 78%–80% to 92%–94%.

Origin and Occurrence of Sodium Nitrate.¹ In the natural

1. For general data on the subject of Chili salpeter, refer to: A. Plagemann, *Der Chilesalpêtre*. Berlin, 1905, pp. 80. K. Jurisch, *Salpeter und sein Ersatz*, Leipzig, 1908, pp. 364. O. Thiele, *Die moderne Salpeterfrage und ihre voraussichtliche Loesung*. Tuebingen, 1904, pp. 46. Semper and Michels, *Die Salpeterindustrie Chiles* (Reprint) Berlin, 1904, pp. 124. H. Polakowsky, *Der Chilesalpêtre und die Zukunft der Salpeterindustrie*, Berlin, 1903, pp. 76. E. Sorel, *Salpêtre, acid nitrique, etc.*, pp. 421–429. E. Frey, *Encyclo. chim.* Vol. 5. B. N. Craig, *Report on nitrification*. Smithsonian Inst. Reports, 1861, pp. 305–18. Natural and artificial formation of nitre. P. Pusey, *On the source and supply of cubic salpêtre, salitre or nitrate of soda, and its use in small quantities as a restorative to corn crops*. London, 1853. Dubuc (pere) *Memoire sur la culture ou fabrication indigene du salpêtre (Nitre de potasse) au moyen de végétaux, etc.* (Extrait) Rouen, 1825, pp. 26. France, *Service des Poudres et Salpêtres. Instruction sur la fabrication du salpêtre*. Paris 1820. Eckhartshausen, -von, *Neue Erfahrungen ueber kuenstliche Salpêtre-Produktion, etc.*, Regensb. 1802, pp. 72. A. Baume, *Observations sur le rapport du Citoyen Guyton . . . sur la question de savoir en quel etat les salpêtres doivent être livrés dans les magasins de la République, et sur le mode d'en juger le titre, etc.*, Ex.: "Annales de Chimie" No. 69, Paris, 1798, pp. 80. V. Requeno, *Saggi sul ustabilimento dell' antica arte de Greci e Romani pittari*. 24 ed. 1 Vol. 2, pp. 131–279. *Saggio storico critico dell' antico nitro*. A. Fortis, *Del nitro minerale, Memoria Storico-fisica*. 1787, pp. 78. J. Weber, *Anmerkungen ueber die . . . Zeugung des Salpeters. Nebst einem Sendschreiben ueber dessen . . . Abhandlung von dem Salpéter-erzeugen, von L. Winzler*. Tuebingen, 1780, pp. 120. France, *Regisseurs Generaux des Poudres, etc. Observations sur le travail des eaux-meres de salpêtre et sur celui des eaux d'atelier*. Paris, 1778. pp. 40. A. Lavoisier, (Collections of papers relating to the State Manufacture of salpêtre and gunpowder), 1777–1792. In his *Oeuvres*, Vol. 5, pp. 391–745. Academie des Sciences, Paris. *Recueil des memories et d'observations sur las formation et sur la fabrication du salpêtre*. Paris 1776. pp. 662. *Kurze und deutliche Vorstellung der edlen Probiér Kunst. . . Nebst einem ausf. Bericht von Salpéter sieden, etc.*, Nuremberg. W. Clarke, *The natural history of nitre*, London 1670, pp. 108. Anon., *Bol. soc. Fomento Fabril (Chile)* 1918, **35**, 116; abst. C. A. 1919, **13**, 2257. Anon., *Chem Trade J.* 1919, **65**, 119; abst. C. A. 1919, **13**, 2420. H. Coc, U. S. P. 1292580, 1919; abst. C. A. 1919, **13**, 998. H. Gale, *Eng. Mining J.* 1919, **107**, 385, 1025; abst. C. A. 1919, **13**, 891, 1903. P. Gonzalez, *Bol. soc. fomento fabril (Chile)*, 1917, **34**, 541, 621; abst. C. A. 1919, **13**, 2258. D. Irvin, *Eng. Mining J.* 1919, **107**, 265; abst. C. A. 1919, **13**, 639. See also C. A. 1918, **12**, 2043. S. Kuroda, *J. Ind. Chem. Japan*, 1918, **21**, 435, 565, 667; abst. C. A. 1919, **13**, 3286. J. Marco, *J. Ind. Eng. Chem.* 1919, **11**, 780; abst. C. A. 1919, **13**, 1903; J. S. C. I. 1919, **38**, 860-A. W. Montgomery & Co., J. S. C. I. 1902, **21**, 146, 290; 1903, **22**, 119; 1908, **27**, 748. M. Prieto, *Bol. minas, Industrias construcciones (Lima, Peru)*, 1917, (2), **9**, 163; abst. C. A. 1919, **13**, 2257. P. Restat, *Bol. soc. fomento fabril (Chile)*, 1918, **35**, 149; abst. C. A. 1919, **13**, 2257. U. S. Com. Rep. Jan. 22, 1919; abst.

occurrence of Chili saltpeter, the world finds, or at least has done so until quite recently, its chief source of combined nitrogen, and the realization that this chief source is limited¹ and is rapidly approaching exhaustion, lends to this problem of nitrogen conservation a peculiarly acute character at the present time. For an industry of such enormous dimensions and importance, and one in which its magnitude is so rapidly increasing, but little authentic text book information is available.

The one region in which this salt has been found in noteworthy quantities is the long arid stretch of highland in Chili lying between the Pacific coast and the base of the Andes mountains, the zone of nitrate-bearing ground comprizing about 200,000 sq. km., of which less than 3% has been surveyed and prospected.² Although rain falls only once in three years, this desert section shows unmistakable indications of a former high fertility. The main nitrate bed is at Tarapaca and is 2½ miles in width by about 250 miles in length, stretching along the eastern slope of the Cordilleras, and from 14 to 90 miles from the sea coast. These deposits are some 500-600 feet higher than the valley of the Tamaragal, the deposits increasing in richness with increasing altitude.

North and south of the main bed above stated are smaller minor deposits, but of insufficient amounts to attract at present commercial exploitation. The sodium nitrate, locally called "caliche," forms a hard mass from 3-6 feet deep, covered to a depth of 5-10 feet with a rock formation, which in turn is covered to a like depth with a fine dry sand. The niter rests upon a bed of clay, and varies in color from white to grey and brown. While the richest beds have been practically exhausted from the viewpoint of the crude methods of working now applied, it has

J. S. C. I. 1919, **38**, 92-R. G. Donnan, Chem. Age, 1919, **1**, 634; abst. C. A. 1920, **14**, 801. L. Sundt, Bol. minero soc. nacional mineria, 1919, **31**, 255; abst. C. A. 1920, **14**, 1100; containing a review of the Pissis, Noellner, Ochsenius, Muntz, Neuton, Plagemann, Van Hise, F. Clarke, Semper and Michels, Gandarilla, and Ghigliotti theories of nitrate formation.

1. S. Loram, Mining Sci. Press, **100**, 125, 180; abst. C. A. 1911, **5**, 975. A. Muntz, Bull. Soc. Chim. 1886, **45**, 340; abst. J. A. C. S. 1886, **8**, 70. J. Singewald and B. Miller, Econ. Geol. 1916, **11**, 103; abst. C. A. 1916, **10**, 2188; Mining Sci. Press, 1916, **113**, 314; abst. C. A. 1916, **11**, 2678. Lunge, "Sulfuric Acid and Alkali," Suppl. Vol., 1917, 44.

2. E. Cuevas, J. Ind. Eng. Chem. 1916, **8**, 195; abst. C. A. 1916, **11**, 1080.

been claimed that there is still sufficient niter present to last the world for at least a century longer, based on the present rate of consumption.

Niter deposits in Colorado,¹ Guyamango in Salvador,² Texas,³ Ferghana, Russia,⁴ in Asia Minor,⁵ Colorado,⁶ and California, have been described but their industrial interest, up to the present is entirely in the future. A detailed description of the Chili and Peru nitrate regions has been given by B. Diaz-Ossa,⁷ P. Martell,⁸ J. Beck,⁹ M. Lamb,¹⁰ Osterreicher¹¹ and I. Hobsbawn and J. Grigioni,¹² from which it appears the method of obtaining the nitrate has not differed essentially in principle from the original processes of lixiviation installed as the result of the original discovery of these deposits by Taddeo-Haenke in 1809. The geological and other details of the origin of these deposits have been exhaustively treated by Langbein,¹³ L. Darapsky,¹⁴ J. Buchanan,¹⁵ Behrend,¹⁶ A. Hartwig,¹⁷ the German Consuls at Valparaiso¹⁸ and

1. M. Sullivan, *J. Ind. Eng. Chem.* 1914, **6**, 532, 586. In this connection see Norton, "Consular Report on the Utilization of Atmospheric Nitrogen," Washington, 1912. W. Newton, *J. S. C. I.* 1900, **29**, 408. W. Crookes, "The Wheat Problem," London, 1905. Thiele, "Salpeterwirtschaft und Salpeterpolitik," 1905. Knox, "Fixation of Nitrogen," London, 1914.
2. "Origin and Occurrence of Sodium Nitrate," Renson, *Chem. Trade J.* 1913, 236. A. Bertrand, *Chim. et Ind.* 1920, **3**, 3.
3. *Oil, Paint and Drug. Rep.* Nov. 23, 1914.
4. *Chem. Ind.* 1916, **39**, 437.
5. *Chem. Ind.* 1916, **39**, 250.
6. Stewart and Greaves, *Bull. 114 of the Agr. Expt. Stat., Utah.*
7. *Orig. Com. 8th Intern. Cong. Appl. Chem.* 1912, **2**, 187; *Rev. gén. sci.* 1912, **23**, 389; *abst. C. A.* 1912, **6**, 2499, 3166. *Bull. Soc. Ind. du Nord*, 1912, **40**, 359; *abst. J. S. C. I.* 1912, **31**, 771.
8. *Zts. Schiess. Spreng.* 1912, **7**, 193; *C. A.* 1912, **6**, 2532; *Chem. Zentr.* 1913, **84**, I, 749; *Chem. Ztg. Rep.* 1912, **36**, 505; *Chem. Ind.* 1913, **36**, 38.
9. *Mining Press.* 1915, 510.
10. *Eng. and Min. J.* **90**, 18; 1915, 811; 1917, **104**, 461; *abst. C. A.* 1910, **4**, 2188; 1917, **11**, 3097.
11. *Prometheus.* 1915, 273.
12. *J. S. C. I.* 1917, **36**, 52; *abst. C. A.* 1917, **11**, 1888. I. Hobsbawn, *Met. Chem. Eng.* 1917, **16**, 253; *abst. C. A.* 1917, **11**, 1264.
13. *Wag. Jahr.* 1871, **17**, 300; 1872, **18**, 290. *Dingl. Poly.* 1879, **232**, 453; *abst. Wag. Jahr.* 1879, **25**, 380; *J. C. S.* 1879, **36**, 1073; *Zts. Chem. Grossgewerbe*, 1879, **4**, 135; *Chem. Ind.* **2**, 235; *Jahr. Chem.* 1879, **32**, 1109. R. Wagner, *Ding. Poly.* 1872, **205**, 75; *Deut. Ind. Ztg.* 1872, No. 17; *abst. Jahr.* 1872, **25**, 980; *J. C. S.* 1872, **25**, 1131.
14. *Chem. Ztg.* 1887, **11**, 752; *J. S. C. I.* 1887, **6**, 545.
15. *J. S. C. I.* 1893, **12**, 128.
16. *Zts. Deuts. Ingen.* 1899, 1199; *Wag. Jahr.* 1899, **45**, 406.
17. *Chem. Ztg.* 1909, **33**, 1162.
18. *Zts. ang. Chem.* 1910, **23**, 1465; *abst. Chem. Ind.* 1910, **33**, 400, 588.

Antofagasta,¹ as well as by the American Consul.²

Formation and Composition of Chili Saltpeter. The distribution of the South American niter is extremely variable. Whereas in a large portion of the territory the top soil contains considerable, but unworkable, amounts, on the other hand, immense districts have been found in which the niter-containing strata assay as high as 95% pure sodium nitrate, from which maximum percentage, all the intermediate gradations to zero per cent. are encountered by the prospector. The caliche strata which are found sufficiently concentrated in sodium nitrate for profitable treatment varies in composition within the following limits: Sodium nitrate, 17%-60%. Potassium nitrate, 2%-5%. Iodine (principally present as iodates) 0.06%-0.25%. Sodium chloride, 20%-30%. Potassium perchlorate, 2%-5%. Moisture 1%-2%. Water insoluble, up to 30%. Small amounts of calcium and magnesium salts as chromates, borates and bromides and bromates are also found, but in too small amounts to admit of their successful commercial recovery.

The theory of the formation of these deposits has never been incontrovertibly established, but the theory of Noeller is generally accepted, and is based on the assumption that the present plateaus of Atacama and Tarapaca were originally below the sea level. Upon being gradually raised enormous amounts of sea weed and other marine vegetation collected within these areas, and the inland sea gradually formed, and the decay gradually of this vast mass of vegetation, aided by nitrifying bacteria, and under the most favorable atmospheric conditions gradually transformed organic nitrogen to inorganic combination, and inasmuch as sodium compounds predominate in marine growth, the sodium salt resulted. This theory is strengthened by the presence in the niter of iodine and potassium compounds in small amounts, and in the ratio roughly corresponding to the soda and potash in the present day kelp.

Extraction and Purification of Chili Saltpeter. The extraction of the niter has until quite recently been a very crude process, consisting in merely leaching the crude niter, filtering off the

1. Chem. Ind. 1911, **34**, 760.

2. Daily Con. Trade Rept. 1908, No. 3327; abst. J. Ind. Eng. Chem. 1909, **1**, 45.

insoluble portion and evaporating the water from the aqueous portion to crystallization by means of the sun, aided towards the close of the evaporative process by artificial heat. J. Price,¹ H. Dartnell,² R. Mueller and the Deutsche Celluloid Fabrik,³ V. Havens,⁴ and H. Sulman, H. Picard and W. Broadbridge⁵ have described processes for obtaining pure sodium nitrate. Filtration of the crude niter solution may be made in a centrifugal filter, W. Gee⁶ having patented such an apparatus which has been extensively used for this purpose. The finished niter as ready for commerce contains about 96% sodium nitrate, and small amounts of potash salts. The processes of T. Roberts and J. Dale,⁷ R. Moore and T. Williamson,⁸ Badische Anilin & Soda Fabrik,⁹ A. Muentz and A. Girard,¹⁰ and A. Taraud and P. Truchot¹¹ for obtaining sodium nitrate are among the more meri-

1. E. P. 24297, 1903; abst. J. S. C. I. 1905, **24**, 276.
2. E. P. 5354, 1895.
3. E. P. 5773, 1914; abst. J. S. C. I. 1915, **34**, 818. See D. Irvin, Mining Sci. Press, 1918, **117**, 109; abst. C. A. 1918, **12**, 2043. Montgomery & Co., J. S. C. I. 1916, **35**, 44. According to R. Dalert (Monatsh. 1908, **29**, 235; abst. J. S. C. I. 1908, **27**, 684), chemical examination of eight specimens "calische" from widely different sources showed that in all cases the portion soluble in water contained calcium, magnesium, potassium, sodium, nitrate, chloride, sulfate and iodate. In most cases, perchlorates also were present; and in the two specimens richest in nitrates, small quantities of chromates were found. In no case did the soluble portion contain bromide, borate, nitrite, ammonia, carbonate, phosphate or iodide. The specimens richest in sodium nitrate contained also much potassium nitrate. Different views as to the causes of the presence of iodate and perchlorate are discussed, the author being inclined to the hypothesis that iodate and periodate are produced by the action of the higher oxides of nitrogen, or of their unstable compounds with ammonia on iodide, and perchlorate by the oxidation of chloride by iodate.
4. U. S. Dept. Com. Repts. No. 68, 1916, 1144; abst. C. A. 1916, **10**, 1696.
5. E. P. 23591, 1912; abst. J. S. C. I. 1913, **32**, 1107; C. A. 1914, **8**, 1334; Chem. Ztg. Rep. 1914, **38**, 170. H. Sulman, H. Picard and Salts Extraction Syndicate, Ltd., E. P. 26056, 1912; abst. C. A. 1914, **8**, 1648; J. S. C. I. 1914, **33**, 24; Chem. Ztg. Rep. 1914, **38**, 230.
6. E. P. 16188, 1911; abst. C. A. 1913, **7**, 5. E. P. 9365, 1915; J. S. C. I. 1916, **35**, 1206.
7. E. P. 2242, 1858.
8. E. P. 1556, 1873. For extraction of sodium nitrate in clays and schists, see F. Duveusart, F. P. 416915, 1910; abst. J. S. C. I. 1910, **29**, 1379.
9. E. P. 10867, 1909; abst. J. S. C. I. 1910, **29**, 425; Chem. Ztg. Rep. 1910, **34**, 315.
10. E. P. 16162, 1907; abst. J. S. C. I. 1908, **27**, 810.
11. E. P. 9461, 1911; abst. J. S. C. I. 1912, **31**, 129; C. A. 1912, **6**, 2826. E. P. 16866, 1911, addn. to E. P. 9461; abst. J. S. C. I. 1912, **31**, 817; C. A. 1913, **7**, 540. See addition of Aug. 20, 1910, to F. P. 425913 of 1910; abst. J. S. C. I. 1911, **30**, 1381; C. A. 1912, **6**, 1969; Mon. Sci. 1913, **79**, 121; Chem. Ztg. 1911, **35**, 529; 1913, **37**, 383.

torious processes which have been proposed from time to time.¹

In the purification of the nitrate heating the solution of nitrate and chloride to 123°–125° for some time at atmospheric pressure causes the sodium chloride to completely precipitate.² C. Uebel³ heats the original niter with sulfuric acid or bisulfate to 100°–130° whereby the impurities are destroyed. A. Schmidt,⁴ Lamb and the Allis-Chalmers Co.,⁵ W. Woodcock and W. Harper,⁶ A. Annandale,⁷ J. Stanley,⁸ and R. Lever have designed various types of lixiviating apparati.⁹ Cost data, production figures,

1. For general survey of patents on sodium nitrate, see the following English Patents: 391, 1861; abst. Mon. Sci. 1878, **20**, 794. 3418, 1862; 301, 2026, 1866; 491, 995, 3183, 1871; 5057, 1878; 1481, 1879; 2816, 1881; 4061, 1883; 12292, 1884; 14441, 1886; abst. Chem. Centr. 1888, **59**, 27. 9122, 1887; 6710, 1889; abst. Mon. Sci. 1896, **48**, 670. 8090, 1890; 16098, 1891; 13655, 13656, 1893; 5354, 1895; 18350, 1899; abst. Chem. Ztg. 1901, **25**, 50; Mon. Sci. 1901, **57**, 152. 3918, 1900; abst. J. S. C. I. 1901, **20**, 263. 23198, 1900; abst. J. S. C. I. 1902, **21**, 185. 23642, 1902; abst. J. S. C. I. 1903, **22**, 696. 24297, 1903; 4796, 1904; abst. J. S. C. I. 1905, **24**, 28. 6143, 1904; abst. J. S. C. I. 1905, **24**, 441. 23909, 1904; abst. J. S. C. I. 1905, **24**, 681. 8721, 1905; abst. J. S. C. I. 1906, **25**, 543. 19189, 1905; abst. J. S. C. I. 1906, **25**, 1044; Mon. Sci. 1908, **69**, 108; Chem. Ztg. Rep. 1907, **31**, 72. 5901, 1906; abst. J. S. C. I. 1906, **25**, 811. 16162, 1907; abst. J. S. C. I. 1908, **27**, 810. 16885, 1907; abst. J. S. C. I. 1908, **27**, 447. 272, 1908; abst. J. S. C. I. 1908, **27**, 685. 24264, 1908; abst. J. S. C. I. 1909, **28**, 708. 10164, 1909; abst. J. S. C. I. 1910, **29**, 1104; F. P. 416224, 1910; abst. J. S. C. I. 1910, **29**, 1380; C. A. 1912, **6**, 1966; Chem. Ztg. Rep. 1910, **34**, 569. E. P. 11274, 1909; abst. J. S. C. I. 1910, **29**, 757. 9884, 1910; abst. J. S. C. I. 1910, **29**, 1157. 10755, 1910; abst. Chem. Ztg. Rep. 1911, **35**, 475. 15525, 1910; abst. J. S. C. I. 1910, **29**, 1380; Mon. Sci. 1915, **82**, 9; Chem. Ztg. Rep. 1911, **35**, 545. For comminuting calcareous saltpeter, see H. Pauling, U. S. P. 1075722, 1913; abst. J. S. C. I. 1913, **32**, 1067; C. A. 1913, **7**, 4050.

2. Process of Gibbs & Co., The Kestner Evaporating Co. I. Hobsbawn and J. Grigioni, E. P. 12474, 12475, 1914; abst. J. S. C. I. 1915, **34**, 715, 799; U. S. P. 1230162, 1230163; abst. J. S. C. I. 1917, **36**, 873.

3. U. S. P. 1082781; abst. C. A. 1914, **8**, 792; Mon. Sci. 1914, **81**, 65. F. P. 451069, 1912; abst. J. S. C. I. 1913, **32**, 602; C. A. 1913, **7**, 3397; Mon. Sci. 1914, **81**, 6; Chem. Ztg. Rep. 1913, **37**, 420. E. P. (with E. Wikander) 28844, 1912; abst. J. S. C. I. 1913, **32**, 700; C. A. 1914, **8**, 1859. E. P. 12475, 1914; abst. J. S. C. I. 1915, **34**, 799. D. R. P. 261874; abst. J. S. C. I. 1915, **34**, 799; C. A. 1913, **7**, 3398; Chem. Zentr. 1913, **84**, I, 463; Chem. Ztg. Rep. 1913, **37**, 412; Wag. Jahr. 1913, **59**, I, 435; Zts. ang. Chem. 1914, **26**, 464.

4. D. R. P. 243949; abst. C. A. 1912, **6**, 2197; Chem. Zentr. 1912, **83**, I, 866; Chem. Ztg. Rep. 1912, **36**, 169; Wag. Jahr. 1912, **58**, I, 422; Zts. ang. Chem. 1912, **25**, 594.

5. U. S. P. 1065053; abst. C. A. 1913, **7**, 2668; Chem. Ztg. Rep. 1913, **37**, 503.

6. E. P. 3918, 1900; abst. J. S. C. I. 1901, **20**, 263.

7. E. P. 3183, 1871.

8. E. P. 4796, 1904; abst. J. S. C. I. 1905, **24**, 28.

9. E. P. 1630, 1873. For the effect of small amounts of iodine in nitric acid and sodium nitrate used for nitroglycerol manufacture, see E. White, J. South Afr. Assoc. Anal. Chem. 1919, **2**, 7; abst. C. A. 1902, **14**, 841.

etc., may be found in the papers of N. Ugalde,¹ M. Prieto² and I. Hobsbawn.³ The Norsk Hydroelektrisk Kvaestof⁴ describe a process for converting sodium nitrate into a fine powder especially suitable as a fertilizer.

Chili Saltpeter Statistics. C. Munroe,⁵ L. Cariola,⁶ H. Le Chatelier and B. Bogitch,⁷ W. Montgomery⁸ and others,⁹ have

1. Bol. Soc. Fomento Fabril, Santiago de Chile, 1915, **32**, 855; 1916, **33**, 18; abst. C. A. 1916, **10**, 1914. According to A. Allen (Eng. Mining J. 1917, **103**, 230; abst. C. A. 1917, **11**, 1020) the caliche or niter-bearing rock is handpicked and all fines are rejected. It is then carted to central loading stations and crushed to a size suitable for leaching treatment. The caliche is delivered to the leaching vats in gable trucks. The vats are rectangular and are grouped in nests. They hold about 80 tons. Each tank has a filter bottom and is lined with steam coils. The solvent liquor used is the mother-liquor from the crystallizing tanks, and is so circulated that the nitrate content of the liquor is gradually enriched by passage from one vat to another. After the liquor is drawn off to the settling tanks, the vat contents are washed with cold water, and the residue left is discharged into trucks and dumped. Vast quantities of slime accumulate under the filter-plate of the tanks, and this carries away a considerable quantity of the nitrate. The strong liquor is tested at every stage of the process with the hydrometer. When the density has reached a satisfactory value, the liquor is drawn off into settling tanks, and the clear liquor is decanted by syphon pipes from these. Lime and guano are used as coagulating agents. The decanted liquor goes to the crystallizing tanks where it is allowed to cool. The stage at which to decant the mother-liquor is ascertained by sounding the crystallizing tank to ascertain the depth of the crystallization. The crystals of NaNO_3 are allowed to dry, and shoveled into trucks and tipped to the sacking house. The NaCl occurring naturally with the caliche is deposited to a considerable extent with the slime in the leaching vats, but a portion goes to the crystallizing tanks. Approximately one-half the nitrate produced is known as "95 and 1%" or "refined" nitrate. This means that the shipped product contains at least 95% of mixed K and Na nitrates, and less than 1% of NaCl . The nitrate content of caliche is generally ascertained by the FeSO_4 method. Actual recoveries of 70%-80% of the nitrate brought to the plants are not uncommon. Any improvements in the process must recognize that the caliche should be crushed only fine enough to permit free penetration of the solvent, and the slime subjected to such treatment as will aid in the recovery of its nitrate content.

2. Bol. Soc. Nacional Minería. Santiago de Chile, 1915, **27**, 510; abst. C. A. 1916, **10**, 1914.

3. Met. Chem. Eng. 1917, **16**, 253; abst. C. A. 1916, **10**, 1264.

4. D. R. P. 276814; abst. Chem. Zentr. 1914, **85**, II, 446; Chem. Ztg. Rep. 1914, **38**, 457; Wag. Jahr. 1914, **60**, I, 374; Zts. ang. Chem. 1914, **27**, 545. R. Fairlie, E. P. 3103, 1872. For physical constants of sodium nitrate, see T. Carnelley, J. C. S. 1878, **33**, 277.

5. J. Ind. Eng. Chem. 1909, **1**, 297; abst. C. A. 1909, **3**, 1914.

6. Bol. Soc. de Fomento Fabril Santiago de Chile, 1917, **34**, 71; abst. C. A. 1917, **11**, 2264.

7. Compt. rend. 1915, **161**, 475; abst. J. S. C. I. 1915, **34**, 1141.

8. J. S. C. I. 1915, **34**, 27.

9. U. S. Com. Rep. 1915, 176; abst. J. S. C. I. Ann. Rep. 1916, **1**, 116. U. S. Com. Rep. 28, Dec. 1915, No. 303; abst. J. S. C. I. 1916, **35**, 304. U. S. Com. Rep. Mar. 7, 1916; abst. J. S. C. I. 1916, **35**, 467. Chem. Trade J. 1908, **43**, 394; abst. C. A. 1909, **3**, 361. Chem. Trade J. 1908, **43**, 533; **44**,

given exhaustive and detailed statistics on the production of this commodity, to the original articles of which the reader is referred.

Potassium Perchlorate. In addition to nitrogen, potassium perchlorate is also found in the original caliche, sometimes to as high as 4%. Recovery of this by fractional crystallization has been worked out by F. Foelsch & Co.¹ and by E. Eger,² advantage being taken of the differential solubility of sodium nitrate and potassium perchlorate in hot and cold water.

Analysis of Sodium Nitrate. The analysis of commercial nitrate of soda involves, in its completeness, the following series of determinations.

Sampling. Take a double handful from each of eight bags in each carload, or in each ten tons, mix thoroughly by hand, and from this select a sample of not less than a kilo. Grind the whole sample as quickly as possible in a mortar to minimize loss of moisture, mix thoroughly, and place in a glass stoppered container.

Moisture. A ten gram sample is gently heated in a platinum crucible to 140° in an air bath with occasional stirring or until the niter just fuses, cooled in a desiccator and weighed. The operation is repeated until a constant weight is obtained. Each loss of 0.1 gm. in weight corresponds to 1% of moisture present.

Insoluble Matter. Fifty grams of the powdered sample is quickly weighed off to an accuracy of at least 0.1 gm. placed in a Gooch crucible or a tared filter paper in a funnel, and washed to exhaustion with warm distilled water, the filtrate being made up to a definite amount and allowed to cool. The crucible (preferably) or tared filter paper is then dried to constant weight in a current of air at 120°. Each 0.1 gm. of residue corresponds to 0.2% insoluble. If it is suspected that there is considerable insoluble organic matter present, the crucible or filter may be

74; abst. C. A. 1909, **3**, 1063. Chem. Trade J. 1916, 519. Chem. Ind. 1916, **39**, 248; 1910, **33**, 758; abst. Oil Paint and Drug. Rept. Sept. 25, 1916; J. S. C. I. 1916, **35**, 1058; Zts. ang. Chem. 1915, **28**, 366; 1916, **29**, 102.

1. D. R. P. 125206, 1900; abst. Zts. ang. Chem. 1901, **14**, 1167; J. S. C. I. 1902, **21**, 51; Mon. Sci. 1902, **58**, 71; Chem. Zentr. 1901, **72**, II, 1101; Chem. Ztg. Rep. 1901, **25**, 989; Chem. Zts. 1902, **1**, 280; Jahr. Chem. 1901, **54**, 392; Wag. Jahr. 1901, **47**, I, 482.

2. D. R. P. 165310; abst. Mon. Sci. 1906, **65**, 148; Chem. Zentr. 1906, **77**, II, 468; Chem. Ztg. 1905, **29**, 1301; Wag. Jahr. 1905, **51**, I, 441; Zts. ang. Chem. 1906, **19**, 931; Zts. Schiess. Spreng. 1906, **1**, 49.

ignited, the difference between the weight of the water-insoluble and the ash representing the insoluble organic portion in the sample.

Potash. Ten gm. are evaporated to dryness with HCl several times in order to completely convert the salts to chlorides, the mass being then dissolved in distilled water and the potassium determined as outlined in Treadwell's "Analytical Chemistry," 2, 49. HCl gas is conducted into the solution which has been concentrated as much as possible, until it has become saturated with the gas, the lower end of the delivery tube being enlarged, and not allowed to dip into the liquid. To each 100 cc. of the solution, 2 cc. of water is now added, the precipitated sodium chloride allowed to settle, and the solution poured through a funnel provided with a platinum filter cone. The precipitated salt is washed three times by decantation with 95% ethyl alcohol, transferred to the funnel, dried by suction and then washed three times more with alcohol.

In the solution there remains the potassium, some sodium, and possible calcium, magnesium and sulfuric acid. The solution is evaporated to dryness on the water bath if possible (or if sulfuric acid is present the last traces of the free acid are removed by means of a free flame), the residue is weighed, and for every decigram of the salt mixture, 3 cc. 2/N HCl added, with more than enough chloroplatinic acid to precipitate all of the potassium, and the liquid is evaporated to a paste. It is then treated with 20 cc. absolute alcohol and well stirred. After standing 5 min., 5 cc. ether is added, the mixture allowed to stand 30 min. under a bell-jar and then filtered. As the residue often contains small amounts of other chloroplatinates, it should be purified as follows: The precipitate is allowed to dry in the air, then dissolved in a little hot water, a few drops of chloroplatinic acid added, and the above operation repeated. The precipitate thus obtained contains all of the potassium in addition to some NaCl and possibly Na_2SO_4 . It is washed with a mixture of ether and alcohol until the liquid passes through the filter completely colorless, after which the precipitate is dried, moistened with hot water, and digested on the water bath with a few drops of pure mercury, constantly stirring with a glass rod until the liquid appears perfectly colorless. This decomposes the potassium chloroplatinate

with separation of platinum, which is readily precipitated.

The mixture is thoroughly dried on the water bath and gently ignited until the Hg is volatilized, the platinum meanwhile being changed to a dense form readily washable by decantation. After cooling the mass is washed with water, the aqueous portion decanted through a filter, and the residual metal washed with hot water, dried and cautiously ignited. The filter is ignited in a platinum spiral, its ash added to the main portion of the platinum in the crucible which is now ignited, and weighed. The weight obtained $\times 0.7612$ gives the amount of KCl, or $\times 0.3994$ gives the corresponding amount of K. The digestion of the potassium chloroplatinate with mercury is carried out in a silica basin.

Chlorides. Ten gm. are dissolved in distilled water and the solution titrated with $N/10$ AgNO_3 , using K_2CrO_4 as indicator. The chloride is calculated as percentage of NaCl on the sample as received.

Perchlorates. A mixture of 10 gm. of sample and 2 gm. CuO is fused in a nickel crucible for 20 min., and when cold the fused mass is treated with distilled water and the aqueous extract titrated with $N/10$ AgNO_3 , using K_2CrO_4 as indicator. The perchlorate equivalent of the chloride corresponding to the difference between the value obtained by this test and that obtained in the foregoing test, is calculated, and after correcting for any iodate which may be present, the result is expressed as percentage of KClO_4 in the sample as received.

Sulfates. Ten gm. are boiled with distilled water and the solution filtered, the filtrate again raised to boiling, and any sulfate present precipitated by the addition of 10 cc. of warm 10% BaCl_2 . The whole is kept hot on a sand bath for an hour to granulate the precipitate, the liquid filtered, washed free from chlorides and ignited in a silica or platinum crucible. After complete incineration of the filter paper, one drop each HNO_3 and H_2SO_4 are added to the precipitate before the final ignition. The result is calculated as percentage of Na_2SO_4 on the sample as received.

Iodates. A mixture of 10 gm. sample and 2 gm. CuO are fused in a nickel crucible for 20 min. When cold, the fused mass is extracted with distilled water and the solution acidified with acetic acid. It is then transferred to a separatory funnel, a few

cc. CuSO_4 solution added and thoroughly mixed with the solution. 20 cc. chloroform are next added and the whole well shaken. The chloroformic layer is next well washed with water and finally titrated with $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$ solution until the pink color is discharged. As usually but a trace of iodate is present, but a few drops of thiosulfate are required. The chloroform layer contains only half of the total iodine resulting from the iodate present in the sample. If there is an appreciable quantity of iodate present, the requisite deduction is made from the value obtained for perchlorate.

Nitrites. Ten gm. are dissolved in distilled water, and a few cc. *m*-phenylenediamine solution added. A brownish coloration shows the presence of nitrites.

Estimation of Nitrate in Chili Saltpeter. Numerous methods leading to results far from concordant have been proposed, and have been arranged by Boeckman in the following summary:

(1) Reduction of the nitrate to nitric oxide. Methods of Lunge (see page 968), of Schlösing-Grandeau¹ as improved by P. Wagner,² and the method of H. Wilfarth.³

(2) Reduction to ammonia in alkaline solution. Method of A. Stutzer,⁴ by reduction by NaOH and aluminium wire. Method of Sievert⁵ by reduction with zinc dust, reduced iron and alcoholic KOH.

(3) Reduction to ammonia in acid solution. Hydrogen reduction method of K. Ulsch,⁶ and the methods of T. Schmitt,⁷ A. Süllwald,⁸ O. Förster,⁹ and the electrolytic methods of K. Ulsch¹⁰ and L. Ingham.¹¹

(4) Reduction to Nitrous acid. Method of F. Gantter,¹²

(5) Determination of the nitric acid by means of the "hydro-

1. *Agrikulturchem. Analyse*, p. 23.

2. *Chem. Ztg.* 1883, **7**, 1710.

3. *Zts. anal. Chem.* 1888, **27**, 411; abst. *Jahr. Chem.* 1888, **41**, 2534.

4. *Zts. ang. Chem.* 1890, **3**, 695; abst. *Jahr. Chem.* 1890, **43**, 2401.

5. See E. Fricke, *Zts. ang. Chem.* 1891, **4**, 240; abst. *Jahr. Chem.* 1891, **44**, 2431.

6. *Chem. Centr.* 1890, **61**, II, 926; *Zts. ang. Chem.* 1891, **4**, 240.

7. *Chem. Ztg.* 1890, **14**, 1410; *Zts. ang. Chem.* 1891, **4**, 240.

8. *Chem. Ztg.* 1890, **14**, 1674.

9. *Chem. Ztg.* 1888, **12**, 1555; 1889, **13**, 229; 1890, **14**, 1674.

10. *Zts. Elektrochem.* 1897, **3**, 546.

11. *J. A. C. S.* 1904, **26**, 1251.

12. *Zts. anal. Chem.* 1895, **34**, 25; abst. *Jahr. Chem.* 1895, **48**, 2771.

'gen deficit," according to the method as perfected by K. Ulsch.¹

(6) Decomposition with HCl. The O. Förster,² G. McGowan,³ H. Neubauer⁴ and R. Bensemann⁵ methods.

(7) Ignition methods of H. Pauli⁶ and Alberti and Hempel.⁷

(8) Soda lime combustion methods of G. Arnold,⁸ A. Houzeau⁹ and E. Boyer,¹⁰

(9) Precipitation with "nitron" according to M. Busch.¹¹

1. Zts. anal. Chem. 1891, **30**, 175; abst. Jahr. Chem. 1891, **44**, 2432.
2. Chem. Ztg. 1890, **14**, 509; abst. J. C. S. 1890, **58**, 1466. Landw. Versuchs Stat. **38**, 165.
3. Chem. News, 1891, **63**, 245; Zts. ang. Chem. 1891, **4**, 557. Compare J. Clennell, Eng. Mining J. 1918, **106**, 660; abst. C. A. 1919, **13**, 16.
4. Zts. anal. Chem. 1900, **39**, 498; abst. J. S. C. I. 1900, **19**, 1040.
5. Zts. ang. Chem. 1906, **19**, 471; abst. J. S. C. I. 1906, **25**, 337. See also J. S. C. I. 1905, **24**, 691.
6. J. S. C. I. 1897, **16**, 494. In this connection see B. Sjollem, Chem. Ztg. 1896, **20**, 1002; abst. J. S. C. I. 1897, **16**, 163. F. Winteler, Chem. Ztg. 1897, **21**, 163; abst. J. S. C. I. 1897, **16**, 358.
7. Zts. ang. Chem. 1892, **5**, 103; abst. Jahr. Chem. 1892, **45**, 2512.
8. Chem. Ztg. 1885, **9**, 533, 715; Rep. anal. Chem. 1885, **5**, 41.
9. Compt. rend. 1888, **100**, 1445; abst. Chem. Ztg. 1885, **9**, 998.
10. Compt. rend. 1891, **113**, 503; abst. Jahr. Chem. 1891, **44**, 2437; Bull. Soc. Chim. 1892, **7**, 155.
11. Ber. 1905, **38**, 856, 861; abst. J. S. C. I. 1905, **24**, 291; J. C. S. 1905, **88**, i, 282, 307. A. Gutbier, Zts. ang. Chem. 1905, **18**, 494; abst. J. C. S. 1905, **88**, ii, 418. M. Busch, Z. Nahr-Genussm. 1905, **9**, 464; abst. J. C. S. 1905, **88**, ii, 418. G. Lunge and E. Berl, Zts. ang. Chem. 1905, **18**, 1681; abst. J. C. S. 1906, **90**, ii, 49. M. Busch and G. Mehrtens, Ber. 1905, **38**, 4049; abst. J. C. S. 1906, **90**, i, 115. M. Busch, Ber. 1906, **39**, 1401; abst. J. C. S. 1906, **90**, ii, 392. Zts. ang. Chem. 1906, **19**, 1329; abst. J. C. S. 1906, **90**, ii, 708. C. Paal and G. Mehrtens, Zts. Nahr-Genussm. 1906, **12**, 410; abst. J. C. S. 1906, **90**, ii, 898. M. Busch, J. prakt. Chem. 1906, **182**, 533; abst. J. C. S. 1907, **92**, i, 259. S. Collins, Analyst, 1907, **32**, 349; abst. J. C. S. 1907, **92**, ii, 349. R. Adam, Bull. Soc. Chim. Belg. 1907, **21**, 229; abst. J. C. S. 1907, **92**, ii, 651. H. Visser, Chem. Zentr. 1907, **78**, I, 302; abst. Chem. Weekblad, 1906, **3**, 743; J. C. S. 1907, **92**, ii, 394. J. Litzen-dorff, Zts. ang. Chem. 1907, **20**, 2209; abst. J. C. S. 1908, **94**, ii, 130. Utz, Zts. anal. Chem. 1908, **47**, 140; abst. C. A. 1908, **2**, 1670. M. Busch and G. Blume, Zts. ang. Chem. 1908, **21**, 354; abst. J. C. S. 1908, **94**, II, 328. A. Hes, Zts. anal. Chem. 1909, **48**, 81; abst. J. C. S. 1909, **96**, ii, 265. H. Franzen and E. Lohman, J. prakt. Chem. 1909, **79**, II, 330; J. C. S. 1909, **96**, ii, 615. M. Busch, Zts. anal. Chem. 1909, **48**, 368; abst. J. C. S. 1909, **96**, ii, 615. P. Booth, Zts. anal. Chem. 1909, **48**, 375; abst. J. C. S. 1909, **96**, ii, 615. C. Paal and A. Ganghofer, Zts. anal. Chem. 1909, **48**, 545; abst. J. C. S. 1909, **96**, ii, 759. L. Radlberger, Chem. Zentr. 1910, **81**, II, 685; from Oesterr. ung. Z. Zuckerind. 1910, **39**, 433; J. C. S. 1911, **100**, 69; C. A. 1911, **5**, 1721. C. Paal and A. Ganghofer, Zts. Nahr-Genussm. 1910, **13**, 322; abst. J. C. S. 1910, **94**, ii, 453. A. Vasilieff, J. Russ. Phys. Chem. Soc. 1910, **42**, 567; abst. J. C. S. 1910, **98**, ii, 1109. S. Seydel and L. Wichers, Zts. ang. Chem. 1911, **43**, 2046; abst. J. C. S. 1911, **100**, ii, 1132. G. Storm, Bureau Mines Bull. 96, 65. W. Cope and G. Taylor, Bureau Mines Tech. Paper 160. R. Escales, "Die Explosivstoffe," 1915, **6**, 351. G. Lunge and E. Berl, Chemisch-technische Untersuchungs Methoden. 1910, I, 391. G. Burrell and F. Seibert, Bureau Mines Bull. 42.

*Determination of Nitrate by Nitrometer.*¹ For this determination, a portion of the sample is partially dried as it is difficult to obtain a representative sample from the powdered wet material. For this purpose about 100 gm. are partially dried by heating in an air oven for 2 hours at 105°. The niter is then quickly powdered in a mortar and transferred to a stoppered bottle which is kept in a desiccator; the actual percentage of moisture in this material being determined as described above, and the results finally calculated back on the sample as received. About 0.4 gm. of the dried sample accurately weighed, is emptied into the dry cup nitrometer, and washed in with 1.5 cc. distilled water. 14 cc. 94.5% H_2SO_4 are then measured out in a graduated cylinder; 8 cc. of this acid are used in 4 successive portions of 2 cc. each for washing down the cup, and the remaining 6 cc. are then added, and the cup well drained into the nitrometer. Decomposition is effected by shaking continuously for 2 min. (checked by a watch) under suction, after which the tube is set up and approximately leveled. After 10 min. the nitrometer is again shaken under slight suction for half a minute and then set up, approximately leveled and allowed to cool. After at least a half hour the tube is accurately leveled by raising or lowering, until on cautiously opening the tap, the drop of sulfuric acid contained therein shows no movement. This condition is best approached from the suction side. The volume is then read and the temperature of a thermometer suspended in close proximity to the nitrometer observed to the nearest 0.1°. The barometer is then adjusted and read, the temperature as recorded by the attached thermometer being observed before touching the instru-

1. In the method of niter analysis of R. Bensemann (Zts. ang. Chem. 1905, **18**, 816; abst. J. S. C. I. 1905, **24**, 691) the sample is dissolved in water, and evaporated to dryness with twice its weight of oxalic acid; to the residue water is added, and the evaporation repeated. This is done from one to five times. The nitrate and chloride present are completely decomposed, the perchlorate and sulfate are not. The residue is now heated to redness in a platinum basin for some minutes, to decompose the perchlorate; it is then dissolved in water, and the solution made up to a known volume. In a portion of this the alkalinity (carbonate) is determined by titration; this corresponds to the nitrate and chloride originally present. A second portion is acidified with nitric acid, and titrated with silver nitrate; this gives the chloride corresponding to the original perchlorate. A third portion (or some of the original substance) is used for the determination of sulfate. The chloride is also determined in a portion of the original substance, and the nitrate is, of course, obtained by subtracting an amount equivalent to this chloride from the joint result given above.

ment,¹ and the tables as shown in Chapter VIII referred to.

The volume of gas in the nitrometer is then re-read, first trying the tap to see if the gas is still in equilibrium, and making any adjustments found necessary. Thermometer and barometer corrections are then made as described elsewhere in this volume. After correcting the volume of nitric oxide to normal temperature and pressure, the percentage of NaNO_3 in the dried sample is calculated, and "solubility" applied to correct for the solubility of NO in H_2SO_4 .

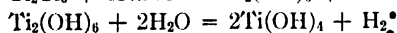
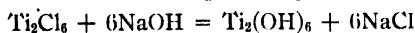
Under the conditions of the test, this amounts to 0.4% of the percentage of NaNO_3 found, i. e., if the sample shows 96.4% NaNO_3 , the solubility correction will amount to 0.4% of 96.4 or 0.38 and the true result will be 96.78%.²

Determination of Nitrate by Titanous Chloride. It has been found that when titanous chloride is added to a strong solu-

1. According to W. Allen (Eighth Intl. Cong. Appl. Chem. 1912, **1**, 19; abst. J. S. G. I. 1912, **31**, 921) by means of complete and comparative analyses, the inaccuracy of the "refraction" (difference) method for the estimation of sodium nitrate in the commercial salt is shown. Direct determination of the nitrogen by a modification of Devarda's process is recommended, the distillation being conducted in a modified form of Knorre's apparatus provided with ground-glass connections. 1 gm. of the sample is treated with 3 gm. of Devarda's alloy (containing 45% of aluminium, 50 of copper and 5 of zinc) in the presence of 25 cc. of a 20% solution of sodium hydroxide, the ammonia produced being absorbed in standard sulfuric acid. When the violent action caused by the introduction of the alloy has subsided, the distillation is continued in a current of air, the flask being heated by immersion in boiling water; before entering the vessel containing the standard acid, the gaseous products are passed through an upwardly inclined, steam-jacketed scrubber (containing glass wool) to prevent alkali "mist" from being carried over. For the titration, a solution of methyl red is used as indicator; the latter being sensitive to carbon dioxide, all the water employed in the process must be boiled before use. The standardization of the sulfuric acid, in terms of sodium nitrate, is effected by a procedure identical with that of the assay, pure potassium nitrate being employed for the purpose. Although not so rapid as the nitrometer method, the process is stated to be more easy of manipulation and is believed to be more accurate, the results of duplications agreeing within 0.15%.

2. J. Clennell (Eng. Mining J. 1918, **106**, 660; abst. C. A. 1919, **13**, 16) has described a modification of the Pelouze method for the determination of nitrate in caliche. The author finds that FeSO_4 is not easily oxidized by the atmosphere, as is commonly supposed. Prolonged boiling of caliche with FeSO_4 does not completely oxidize the ferrous to ferric unless the mixture contains a considerable concentration of H_2SO_4 . When chlorides are present in the caliche, they also are reduced, causing high results. They also reduce KMnO_4 in the final titration unless the decomposed sample is sufficiently diluted. A standard solution of FeSO_4 with the necessary amount of free H_2SO_4 does not keep owing to the formation of an insoluble precipitate. He advises a solution only slightly acidified. Since the boiling cannot be hurried, a determination required about 45 minutes.

tion of NaOH, the reaction which ensues results in precipitation of white titanic hydroxide and the liberation of H. The reaction proceeds in the following two steps:



The first reaction results in the precipitation of black titanic hydroxide, which decomposes into nascent hydrogen and white titanic hydroxide. If the reaction be performed in a solution containing nitric acid, the H reduces the latter, with the formation of ammonia ($\text{HNO}_3 + \text{H}_2\text{NH}_3\text{H}_2\text{O}$). The ammonia thus produced may be collected in standard acid, the quantity of nitric acid originally present being calculated from the amount of acid neutralized.

In practice 20 gm. of the powdered sample is weighed into a distilling flask and about 16 gm. NaOH added, together with 75 cc. water. The solution is brought to a boil and 20 cc. of 15% solution of titanous chloride added by means of a separatory funnel fitted to the flask. The latter is connected to a Kjeldahl which leads into a receiver containing 20 cc. $N/10$ H_2SO_4 . The flask is boiled for 20 minutes, disconnected, and the distillate titrated back with $N/10$ NaOH.

Recovery of Niter from Chili Saltpeter Bags. In this plant are washed the empty bags from the niter sheds, the double object being the recovery of the sodium nitrate, and the production of a clean and merchantable bag. There is, in addition, the danger that if the bags are not washed, they may spontaneously ignite when packed and stored.¹

The bags are first boiled in a cylindrical container, and are then passed successively through a series of washing troughs counter-current to a stream of hot water, the bags being hand transferred from the boiler to trough, and from trough to trough, by hand. Usually four troughs are provided, the bags after leaving the first trough being centrifugally wrung, and finally dried, the "fbis" dryer having been extensively used for this purpose in England.

The hot water supply enters the system at the last trough and flows forward to the boiler, gradually increasing in nitrate

1. Data in this topic has been drawn from the report on H. M. Factory, Queen's Ferry, Acid Section, V. Gloag and J. Riley, 1918.

concentration on the way. From the boiler, when sufficiently concentrated, it is blown by air to an overhead tank, from which it passes to a concentrator as of the Kessner or Zarembo type, and is delivered to mild steel crystallizing pans.

The crystals are drained, sometimes centrifugalized, bagged, and sent to the niter storage house, the mother-liquor being returned to the circulating system until it becomes too foul for profitable utilization, when it is discarded.

In the unwashed bag store, the bags are received in trunks, unloaded, brushed to remove adhering crystals and conveyed by belt or trolley to the boiler. The latter comprises a perforated steel drum of 3' diameter and 4' deep, with 2" perforations at 4" centers, and containing a perforated steam coil. Here the bags are boiled, then pressed, as by a pneumatic piston press of the Douglas-Fraser pattern, in order to remove as much as possible of the concentrated niter liquor. From the boiler, the bags are removed to the troughs, a convenient size being 12' \times 4' \times 3' deep. The last trough is fed with water from an overhead tank. From the last trough, the bags pass to an electric or belt driven laundry centrifuge, of 36"-40" basket, making 1100-1200 revolutions per minute, the drainings being pumped to the next to last trough.

The Ibis type of dryer has been used at the Queen Ferry Plant, England, and are 20' \times 10' wide, the bags at the feed end being clipped to traveling rods so arranged that when the rod reaches the delivery end they are automatically released. The drying is done by hot air generated by a 30" fan blowing air over a cast iron steam radiator situated at the delivery end of the apparatus. The capacity of each drier is about 200 bags, and will dry 120 bags per hour.

The clean bags are sorted and stored in a fire-proof building. The liquor from the boilers is circulated until the gravity is sufficiently high to admit of profitable concentration. When this point is reached, it is blown through a filter press to remove extraneous impurities into the main feed tank for the evaporators. The feed tank to the evaporators is of mild steel construction, lagged, and fitted with overflow and discharge pipes. The water tank feeding the last trough is preferably of the same dimensions, and acts as a catch-all for the condensed water from the steam

traps. This method is said to have proven quite efficient.

In the Kestner form of evaporator, the horizontal type consists of a bank of four tubes 16' 6" long and arranged with concentric steam pipes. The concentrated liquor is fed in at the bottom of the nest of tubes, the steam entering at the top on the counter-current principle. During its passage through the tubes the liquor is concentrated and is finally discharged into a cast iron separator, the steam escaping to the atmosphere, and the liquor running to the launders.

The concentrated liquor from the evaporator is distributed into one or more water-cooled pans to permit of crystallization. These may be 15' \times 4' 9", being 9" deep for 10' of their length and grading through the last 5' down to a depth of 1". They are constructed of mild steel plates one-fourth inch thick, and each is set in a cooling pan 15' 3" \times 5' 3" \times 12" deep, fitted with water overflow. After the niter has crystallized out, it is drained and the mother-liquor returned to the circulation tank by means of a steam injector.

The washing yields a bag containing about 5% NaNO_3 and 10% H_2O , about 0.65 long tons sodium nitrate per day with a water content of 10.5% from the efficient working of a plant handling 15000 bags per week. The average NaNO_3 content of unwashed bags is about 29%. Bags may be charged into the boiler at the rate of about 50 per hour it being expedient to have at least one spare boiler. The complete cycle of operations in the boilers takes about one hour, the washing operation in the troughs being phased synchronously. An evaporator should be used which will evaporate 220-240 cu. ft. of liquor per 24-hour day with a 3% NaNO_3 content, and deliver 150-160 cu. ft. per day with a 50% NaNO_3 content. Where four troughs are employed in the washing cycle, the gradient backwards to the boiler is about as follows: Trough 4, 15.2% NaNO_3 , temperature 36°; trough 3, 19.6%, 33°; trough 2, 24.1%, 41°; trough 1, 30.6%, 75°; and boiler, 35% NaNO_3 , temperature 103°.

Manufacture of Nitric Acid from Sodium Nitrate. In the United States, practice differs as to whether the Chili saltpeter is or is not dried before introduction into the nitric acid retort, but the present tendency is to pre-dry the niter on account of the materially greater yield of more concentrated nitric acid.

C. Claessen¹ advocates the briquetting of the niter, claiming that the distillation of nitric acid from a mixture of nitrate and vitriol is rendered more uniform, and blockage in the retorts is avoided. Where "green soda" (undried niter) is used, the amount of sulfuric acid per charge is correspondingly increased to take care of the additional water introduced from the niter moisture. It is a peculiar observation, but satisfactory results appear not to be attained when the moisture in the niter is counterbalanced by the use of more concentrated vitriol.

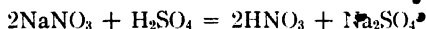
It has also been advocated to carry the drying of the niter to the point of fusion, the impurities which fuse at a higher temperature rise to the top and may be skimmed off and discarded, or worked over as a separate process. The main point of apparent advantage in this suggestion is at factories which also manufacture black powder and other explosives containing sodium nitrate. The fused mass may then be ground and sifted, and the finer portions used for powder. Where fused niter is used for nitric acid manufacture, the still may be run to dryness and a nearly theoretical yield obtained.

B. Dunn² and G. Loos³ have called attention to the dangers from stored niter, which, when kept in a very humid atmosphere deliquesces on the surface, the bag becoming saturated with a solution of NaNO_3 . If the bag again dries it becomes highly inflammable, and great care should be exercised in handling such bags. It should never be stored in contact with wood, nor in the neighborhood of other combustible materials as sulfur or sugar. Used bags should not be stored for any length of time, but should pass through the bag recovery plant as fast as emptied. The production of iodine from nitrate liquors,⁴ and the hygroscopicity of NaNO_3 ,⁵ are important problems where large amounts of Chili niter are dealt with.

The theory requires 85 parts absolute sodium nitrate to 49 parts H_2SO_4 , to yield 63 parts HNO_3 and 71 parts Na_2SO_4 , where

1. E. P. 6102, 1915; abst. J. S. C. I. 1915, **34**, 1009; C. A. 1916, **10**, 2620; Mon. Sci. 1918, **85**, 17; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 115.
2. B. E. Accident Bull. 1919, No. 44; abst. C. A. 1919, **13**, 2129.
3. Arch. Suikerind. 1918, **26**, 1893; abst. C. A. 1919, **13**, 2738.
4. W. Montgomery & Co., Sept. 28, 1903; abst. J. S. C. I. 1903, **22**, 1157. W. Newton, J. S. C. I. 1903, **22**, 469; abst. Jahr. Chem. 1903, **56**, 323; Chem. Centr. 1903, **74**, II, 158; Chem. Zts. 1903-1904, **33**, 40; Rep. Chim. 1903, **3**, 417.
5. E. C. I. Research Report No. H. 72, March 16, 1912.

the following is the equation which is substantially carried out:



In practice, however, it is customary to use a slight excess of sulfuric acid over the calculated amount, in order to increase the fluidity and flowing of the niter cake (NaHSO_4), although the method of operating the process governs in a great measure what this excess shall be. It always is reduced to the minimum consistent with maintaining a satisfactory yield of nitric acid. For a two-ton retort, 3600 lbs. dried niter and 3800 lbs. 92% vitriol have been found to give a maximum yield when operated efficiently.

From the steel reinforced bee-hive niter storage house, the NaNO_3 is weighed out, and run in on trucks on a narrow gauge track, the track being built directly over the nitric stills,¹ it being dumped directly into the still through the man-hole by either tilting the car, or through a discharge bottom. The acid is run in the retort after the niter has been added. E. Schwarz and A. Bauschicher² use waste sulfuric acid from paraffin manufacture. The acid is either run in by gravity, or an apparatus of the C. de Preville type³ may be employed. The retort is of cast iron, usually tubular with rounding bottom, with man-hole on top, and a 3-inch outlet at the rear bottom for the niter cake. A preferred form of retort which was used in immense quantities during the past few years, is that shown in Figs. 42 and 43, and made by the Buffalo Foundry and Machine Co., of Buffalo, New York. These retorts are made in sizes up to a maximum

1. Societa Anonima L. Vogel, E. P. 6846, 1904; abst. J. S. C. I. 1904, **23**, 1088. Sadtler, Chem. Trade J. **34**, 517.

2. D. R. P. 46101; abst. Wag. Jahr. 1889, **35**, 23; Chem. Centr. 1889, **60**, I, 688; Bied. Tech. Chem. Jahr. 1888-1889, **11**, 476. The nitric acid still of R. Manser, is described in U. S. P. 1320080, 1919; abst. C. A. 1920, **14**, 313. See C. Kippenberger, Ber. Pharm. Ges. 1919, **29**, 391; abst. C. A. 1920, **14**, 313.

3. E. P. 128061, 1918; abst. J. S. C. I. 1919, **38**, 561-A. In this method the acid or other liquid is admitted by gravity to a vessel through a non-return valve and expelled by compressed air through a second non-return valve. The pressure air is admitted or exhausted by means of two cocks which are rotated together by a 4-tooth ratchet in such a manner that one is open while the other is closed. The ratchet is rotated 90° at a time by means of a pawl operated by a piston which is pressed down by compressed air and returned by a counterweight. The movements of the piston are slow and are controlled in either direction, as is also the rate of expulsion of acid, by three-air-regulating valves, an automatic valve being provided to permit the piston to rise again after reaching the bottom of its stroke. One motor may serve two sets of acid vessels and cocks, thus producing a fairly constant delivery of acid.

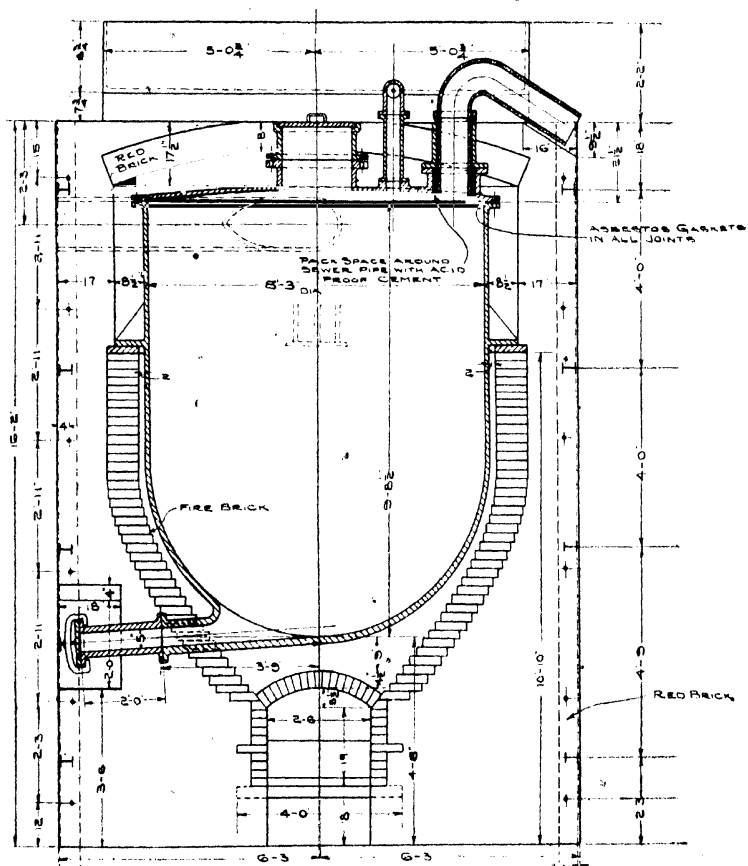
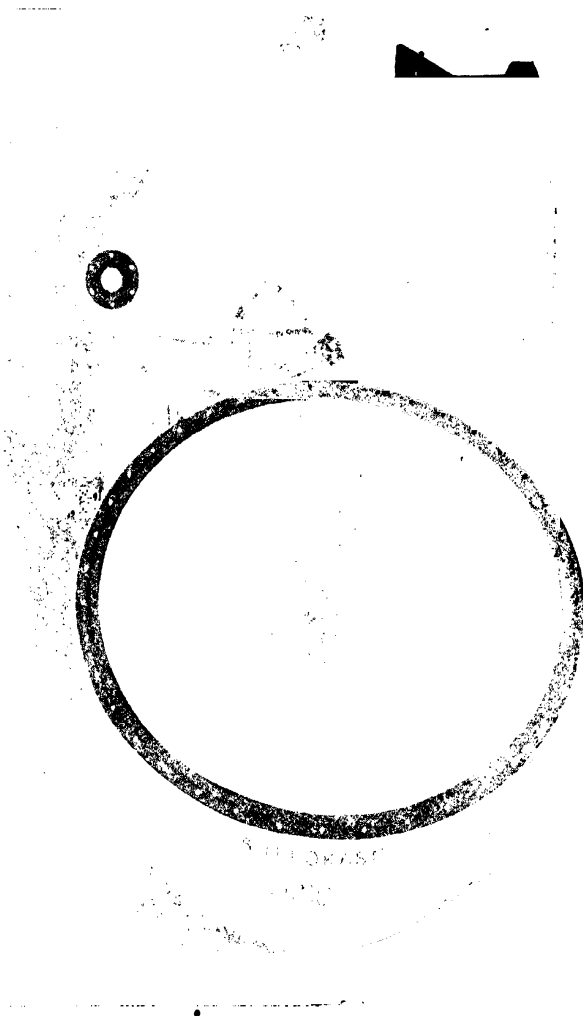


FIG. 42.—NITRIC ACID STILL (BUFFALO FOUNDRY & MACHINE CO.)

FIG. 43.—NITRIC ACID STILL (BUFFALO FOUNDRY & MACHINE CO.)



charge of 10,000 lbs. of sodium nitrate and are cast in one piece. Where a two-piece retort is used the parts are fastened together with bolts, leaving a space of about one-fourth inch, which is filled in with iron borings soaked in sal-ammoniac, the borings being driven in both from the inside and outside. This caulking will usually last for a year. It is preferable that the two saddles on the top of the retort where the sodium nitrate is charged and the nitric acid vapors are delivered to the condenser should be cast on the still instead of being fastened with stud bolts, as the nitric acid fumes attack the iron rust joints, causing leaks.

As the niter falls into the retort it naturally assumes the shape of a cone with the apex upward. By means of a long handle spoon shovel, such as is used for digging post holes, the sodium nitrate in the retort is carefully smoothed off by hand. This is done in order to prevent the lower layer of nitrate being converted into nitric acid, and the big, solid, cone-like mass becoming hard and falling after the lower mass becomes hot, thus resulting in an evolution of nitric acid vapors much greater than the condensing apparatus can handle.

The sulfuric acid required for a charge may be measured off in a flat iron crock fitted with a gauge glass running parallel with the sides of the crock. The use of spent acid in the retorts increases the lower nitrogen oxides, and has other disadvantages. After the still has been started, the contents of the still is not stirred nor agitated in any way.

Pea coal is used as fuel, about 150 lbs. being required per ton of nitric acid distilled, although the fuel consumption is subject to considerable variation, depending upon the type of retort used, speed of working off the charge, and efficiency in firing. The fires are run slowly at first for three or four hours, but towards the end of the process the heat is increased so the interior of the retort and the temperature of the issuing gases will be about 180°. Slow and uniform firing and the use of a distilling acid of not over 93.5% H_2SO_4 will materially assist in lowering the percentage of lower nitrogen oxides.

The Du Pont de Nemours Co. heats by means of an oil-bath.¹ Modifications of the above type of acid retorts have been de-

¹ U. S. P. 1140351, 1149711, 1915; abstr. J. S. C. I. 1915, **34**, 960; Chem. Ztg. Rep. 1916, **40**, 132; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 115.

scribed by E. Manser,¹ E. Hart,² C. Curtis,³ C. Bolz,⁴ A. Cumming,⁵ and others.⁶ Acid-resisting apparatus has also been described by E. Poste,⁷ General Chemical Co.,⁸ N. Swindin⁹ and W. Carnell.¹⁰ The retort furnaces of W. Fletcher,¹¹ and of M. Prentice¹² have been used for nitric acid distillation.

The still may be connected to the condensation apparatus by means of a 4" vitrified sewer pipe containing a 90° elbow bend, the end of the pipe from the retort being luted into the side near the bottom, of a 22-hole Hart condenser or manifold upright. This manifold, which is of vitrified stoneware, contains a 4" opening on one side, and on the other side, 22 equal openings arranged in two segments, one above the other, the lower being twelve holes, and the upper, ten. Into each of these holes is luted 22 glass tubes by means of shredded asbestos. At the other end of the 22 tubes, which are 3" internal diameter, is a similar manifold, but without the 4" opening on the opposite side. The manifold nearer the retort contains two partitions, the first being between the 12-13 tube, and the second between the 17-18 tube. The upper ten tubes are set perfectly level, i. e., at right angles to the two manifold uprights. The lower twelve tubes tip 1½" in their length (6') towards the retort.¹³ The details of this form

1. Can. P. 190284, 1919; abst. C. A. 1919, **13**, 1410.
2. Met. Chem. Eng. 1918, **18**, 534; abst. C. A. 1913, **12**, 2043.
3. U. S. P. 1311051; E. P. 121855, 1918; Can. P. 193579, 1919; abst. J. S. C. I. 1919, **38**, 107-A; C. A. 1919, **18**, 893, 2305; 1920, **14**, 106.
4. E. P. 28941, 28942, 1910; abst. J. S. C. I. 1911, **30**, 735.
5. J. S. C. I. 1919, **38**, 31-T; abst. C. A. 1919, **13**, 1019.
6. V. Majerus, J. Errington and A. Hammond, E. P. 117233, 1917; abst. C. A. 1918, **12**, 2418; J. S. C. I. 1918, **37**, 496-A.
7. J. Amer. Ceram. Soc. 1919, **2**, 62; abst. J. S. C. I. 1919, **28**, 287-A; C. A. 1919, **13**, 1136.
8. U. S. P. Appl. Nov. 3, 1917; E. P. Appl. 7869, 1919; abst. J. S. C. I. 1919, **38**, 238-A.
9. Chem. Trade J. 1916, **59**, 323; abst. J. S. C. I. 1916, **35**, 1095; C. A. 1917, **11**, 1; Met. Chem. Eng. 1916, **15**, 647.
10. J. Ind. Eng. Chem. 1916, **8**, 922; abst. C. A. 1917, **11**, 143. Iron Age, 1916, **98**, 182; abst. C. A. 1916, **10**, 2866. Chem. Trade J. 1916, 182.
11. U. S. P. 1156595, 1915; abst. C. A. 1915, **9**, 3334; J. S. C. I. 1915, **34**, 1197.
12. U. S. P. 527718, 1894.
13. The object of this is so the condensed nitric acid will run back towards the retort, and in doing so will condense some of the hottest gases coming from the retort, thus resulting in a purer nitric acid, and one that is substantially free from hyponitrous acid. Each condenser tube has placed over it for its entire length, a piece of readily absorbent cloth as cheese cloth or fine muslin, over which constantly trickles a stream of water, the object of the cloth being to more evenly distribute the water, and thus increase the condensation of nitric acid. At the top of the condenser is a half-inch

of condenser are shown in Figs. 44 and 45.¹ The nitric acid vapors pass through this condenser into two 5-hole stoneware Hart manifold condensers, connected by five 6' phenestrated

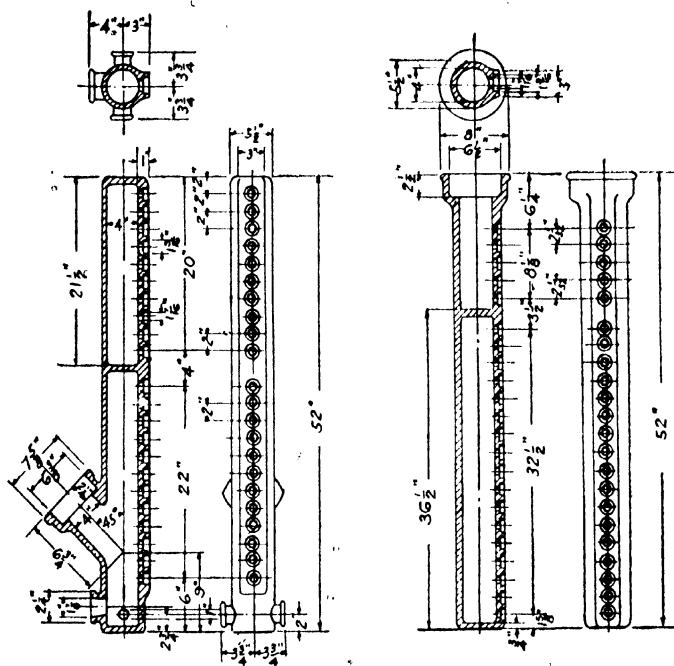


FIG. 44.—HART NITRIC ACID CONDENSING MANIFOLD

iron pipe, in which is bored $\frac{1}{8}$ holes every 3" of its distance, and through which water trickles on to the upper of the 22 glass tubes, and so on down on the others, until finally it empties into an iron trough under the lower tube. This trough has a flat bottom, being about 2" wide at the bottom, 3" deep and with sides flaring upward.

In the phenestrated tubes, one end of each is closed while the other end remains open, the closed end of one is directly below the open end of the one next above it. Thus the liquid which runs out of the open end of one tube, drops into the oval top opening of that end of the tube just below it, the end of which, however, is closed. The condensing and cooling system, therefore, required 27 separate tubes, 22 of which are alike, and 5 are similar, and these 27 tubes are each luted to the 4 manifolds by means of asbestos cement or packing. From the phenestrated glass tubes, the condensate runs directly into a glass adapter, and this again into a convenient glass tube leading to the receiver.

¹ E. Hart, U. S. P. 525761, 1894; 603508, 1898; E. P. 17289, 1894; 29391, 1910; 27654, 1912; abst. J. S. C. I. 1894, **13**, 1197; 1912 **31** 477; 1913, **32**, 817; C. A. 1912, **6**, 1387.

glass tubes, known collectively as the "cooling system" in contradistinction to the 22-tube manifold, designated as the "condensing system." From this the now thoroughly cooled nitric vapors are run into any suitable receiver, either with or without

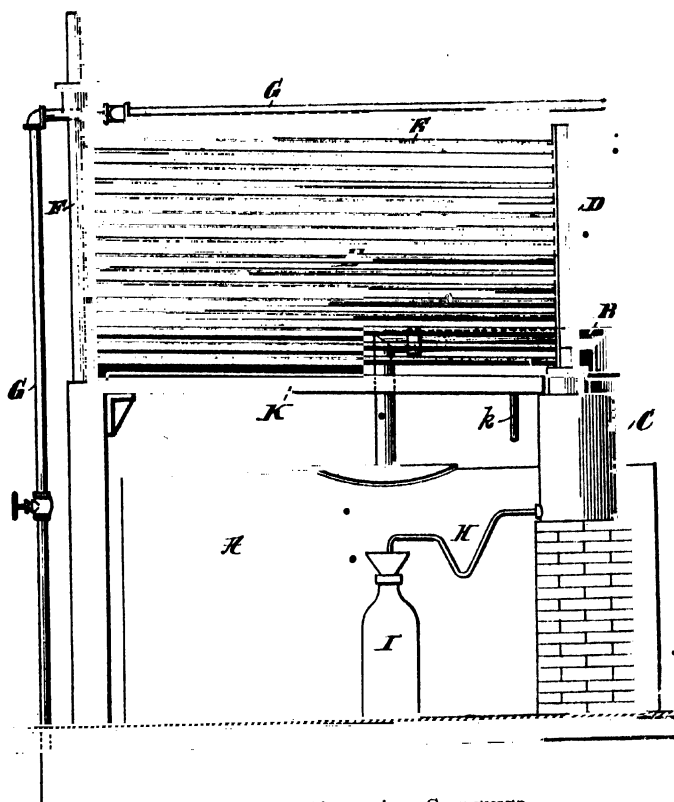


FIG. 45.—HART NITRIC ACID CONDENSER

the interposition of an acid condensing tower, and the process is finished.

At the commencement of the process the nitric acid has a sp. gr. of 1.35, distillation being continued until the gravity is reduced to 1.20. The heating is then discontinued, and the niter cake at once run out, before the still has had an opportunity to

cool. The contents of the retort are poured into heavy, shallow iron pans, and after cooling, broken up into convenient size by means of a sledge hammer. It is customary to so arrange the receiving apparatus that fractions of different densities may be separated, the more concentrated acid being allowed to flow into one receiver, and the weaker nitric acid into a separate one.

In the A. Hough condenser for nitric acid vapors,¹ the condenser comprises a casing built up of flanged sections bolted together to constitute an upright apparatus. The sections are provided at their meeting places at opposite ends with meeting accurate recesses, in which pipes for the condensation are held. The joints between the pipe sections are placed outside the sectional casing, and baffles in the casing cause a tortuous flow of cooling fluid through it around the condensing pipes.

In the B. Dawson method,² the gases from the retorts and condensers are treated in an empty tower with an air spray, and water produced by admitting compressed air by a nozzle opening below the level of the water in the bottom of the tower.

O. Guttman³ combines an inclined pipe subdivided into chambers, with tubes, bulbs and arc pipes, connecting adjoining chambers on top, and with elbow pipes connecting adjoining chambers at the bottom. In the apparatus as devised by W. Hayhurst,⁴ a vessel of prismatic form, having a cross-section of triangular or other form is provided with large cooling surface. In one form the cross-section may be of inverted T-shape. A series of such vessels is arranged in a sloping tank, the vessels being connected at the bottom.

According to R. Rosenthal⁵ the hot gases generated during the manufacture or distillation of nitric acid, hydrochloric acid, or the like, are passed upwards through a condensing tube, of which the lower portion is air-cooled and the upper portion is

1. U. S. P. 1312118, 1326267, 1919; abst. C. A. 1919, **13**, 2576; 1920, **14**, 601.

2. E. P. 120869, 123344, 1919; abst. C. A. 1919, **13**, 1519; J. S. C. I. 1919, **38**, 252; Mon. Sci. 1919, **86**, 41, 43.

3. U. S. P. 472498, 1892; abst. J. A. C. S. 1892, **14**, 119. Chem. Ztg. 1905, **29**, 934; abst. J. S. C. I. 1905, **24**, 934; Chem. Centr. 1905, **76**, II, 1055; Jahr. Chem. 1905-1908, I, 1793; Meyer Jahr. Chem. 1905, **15**, 373. J. S. C. I. 1908, **27**, 667; abst. C. A. 1908, **2**, 2849; Meyer Jahr. Chem. 1908, **18**, 349; Chem. Zentr. 1908, **79**, II, 1068.

4. E. P. 114706, 1917; abst. C. A. 1918, **12**, 1521; J. S. C. I. 1918, **37**, 289-A.

5. D. R. P. 314293, 1918; abst. J. S. C. I. 1920, **39**, 20-A.

cooled by a stream of water. The gases are partially cooled in the lower portion and condensation is effected in the upper portion; the condensed liquid flows down the tube and meets the ascending stream of hot vapor whereby certain impurities, *e. g.*, nitrogen peroxide in the case of nitric acid, are removed. The purified liquid passes out at the lower end of the tube, through a coil cooled by the overflowing of cooling water from the upper portion of the condensing tube, and into a receiver; uncondensed gases leave the tube at the upper end and pass into an absorption apparatus.

J. Lang¹ passes the crude nitric vapors into a receiver kept warm enough to volatilize the impurities, but cool enough to condense the pure nitric acid. J. Skoglund² passes nitric acid vapors into chambers containing broken acid-proof material, condensing, and allowing the condensed acid to run again over the broken material to remove impurities. H. Nielsen³ has patented a filling material for towers, and formed of a 3-sided hollow body of twisted contour but with the top and bottom edges parallel with each other, to facilitate regular piling.

The theory of absorption towers for nitric acid manufacture has exhaustively been studied by J. Partington and L. Parker.⁴ In the acid fumes conveyor of A. Porter,⁵ the retorts in which the reactions occur are connected by flues to a header having one or more outlets at suitable points, and connected with tanks in which the nitric vapors may be condensed. Special vessels for storing the nitric acid have been described by W. Hayhurst,⁶ W. Russell,⁷ Brookes Chemical Co. and N. Brooke,⁸ and I. Wolf.⁹ The H. Weidig and R. Remmey nitric absorption tower¹⁰ is

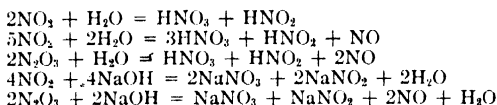
1. U. S. P. 477375, 1892; abst. J. A. C. S. 1892, **14**, 165.
2. U. S. P. 591087, 1897; E. P. 18362, 1888; F. P. 194905, 1888; abst. Mon. Sci. 1889, **34**, 756; J. S. C. I. 1889, **8**, 478.
3. U. S. P. 1307635, 1919; abst. C. A. 1919, **13**, 2265.
4. J. S. C. I. 1919, **38**, 75-T; abst. C. A. 1919, **13**, 2109.
5. Can. P. 191254, 1919; abst. C. A. 1919, **13**, 1781.
6. E. P. 122661, 1917; abst. C. A. 1919, **13**, 1752; J. S. C. I. 1919, **38**, 164-A.
7. U. S. P. 1315241, 1919; abst. J. S. C. I. 1919, **38**, 805-A; C. A. 1919, **13**, 2785.
8. E. P. 129709, 1917; abst. C. A. 1919, **13**, 2786; J. S. C. I. 1919, **38**, 670-A.
9. U. S. P. 1285537, 1918; E. P. 113992, 1918; abst. J. S. C. I. 1918, **37**, 229-A.
10. E. P. 1082, 1888; abst. J. S. C. I. 1888, **7**, 322; Wag. Jahr. 1888, **34**, 468; Mon. Sci. 1908, **60**, 105.

at the present time, but little used in the United States.

C. Volpéy¹ has shown that the frothing in the niter process, of nitric acid manufacture takes place ordinarily only in the last stage, but practical experience has demonstrated that often it is in the earlier part of the process, while the retort is nearly full, that frothing is most prone to occur.

The figures for nitric acid production in all H. M. Factories (England) for the thirteen-week period ending December 29, 1917, are as follows: Sulfuric acid (as 100%), 36588.8 (long) tons; NaNO₃ used (as 100%), 37020.9 tons; ratio H₂SO₄/NaNO₃, 0.9888; acidity of niter cake (calc.), 31.4%, (found) 26.0%.

The A. Classen process of nitric acid manufacture from nitrogen oxides,² is represented by the following equations:



The conversion of nitrogen oxides is obtained, according to the invention, by carrying out the oxidation in the presence of suitable catalyzers arranged on suitable supports.

The acid siphon of W. Szigeti,³ and the method of packing the pistons of nitric acid vacuum pumps as described by S. Dreyfus,⁴ are of interest in this connection.

In the manufacture of nitric acid, and in general in handling mixtures containing nitric acid, danger from poisoning should be continually borne in mind. Due to the care which is bestowed on the construction and ventilation of modern chemical plants where noxious fumes are prevalent, the danger from fume poisoning at present, is not as acute as formerly. Notwithstanding the fact that accidents of this nature have been reduced to a minimum,

1. J. A. C. S. 1891, **13**, 246; 1901, **23**, 489; 1902, **24**, 222; 1903, **25**, 406; J. S. C. I. 1892, **11**, 342; 1901, **20**, 544, 1189; 1903, **22**, 780; J. C. S. 1892, **62**, 941; 1901, **80**, ii, 600; 1902, **82**, ii, 394; Bull. Soc. Chim. 1892, **8**, 881; 1902, **28**, 625; Rep. Chim. 1901, **1**, 435; Chem. Centr. 1892, **63**, I, 348; 1901, **72**, II, 508, 616; 1903, **74**, II, 532; Chem. Tech. Rep. 1892, **31**, I, 232; Chem. Zts. 1903-1904, **3**, 164; Jahr. Chem. 1892, **45**, 2694; 1901, **54**, 262, 283; 1903, **56**, 382; Meyer Jahr. Chem. 1892, **2**, 338; 1901, **11**, 319; Wag. Jahr. 1892, **38**, 357; Trans. Amer. Electrochem. Soc. 1903, **3**, 285.

2. E. P. 18065, 1915; abst. C. A. 1917, **11**, 1889.

3. Chem. Ztg. 1915, **39**, 122; abst. J. S. C. I. 1915, **34**, 278; C. A. 1915, **9**, 557.

4. E. P. 102527, 1916; abst. J. S. C. I. 1917, **36**, 201.

it is practically impossible to entirely prevent their recurrence.

When care is taken to remove fumes by efficient forced draught ventilation little danger is present so long as the processes operate normally. When poisoning has occurred, however, the patient should be immediately removed to the open air, kept warm, and oxygen inhalation, aided by small doses of chloroform, immediately administered, the oxygen treatment being continued until all danger apparently has passed. In this manner decomposition of the hemoglobin of the blood is reduced to a minimum, and unless the case is of unusual gravity, the continued administration of oxygen is sufficient.

Where large quantities of nitrous fumes have been inhaled, congestion of the lungs results, and during the second stage great care must be exercised that no hemorrhage occurs from coughing, due to irritation of the larynx and throat. Severe cases are manifested by obstruction of the air passages, difficulty in breathing, severe pectoral pains, swelling of the mucous membrane, difficulty in deglutition and articulation and cardiac disturbances.

According to L. De Blois¹ the best means of preventing poisoning by nitrous fumes in works where nitric acid and mixed acid are used, is the provision of efficient ventilation. In the E. I. du Pont de Nemours Powder Co.'s works, the fumes are removed by means of large down-draught exhaust fans. The earthenware pots in which cotton is nitrated are placed in partial enclosures over slatted openings through which the fumes can be drawn at a velocity of about 830 ft. per minute between the slats with full opening, and in some cases 2500 ft. per minute close to the top of the pot. Before an efficient exhaust system was developed, good results were obtained by spraying ammonia or ammonium carbonate solution directly into the air by compressed air atomizers. Each atomizer consumed about 2½ cu. in. of ammonia solution of 30° Bé. (sp. gr. 0.875) per hour at an air pressure of 25 lbs., and this was sufficient to neutralize "rather dense" fumes over an area of about 252 sq. ft. of floor surface. Respirators are not generally very satisfactory. The most efficient type was an aluminium respirator having an exhaust valve and inflated rubber face-cushion, and with the usual sponge replaced

1. J. Ind. Eng. Chem. 1916, **8**, 1162; abst. J. S. C. I. 1917, **36**, 44; C. A. 1917, **11**, 188.

by a disc of "Filtros," $2\frac{1}{2}$ in. diam. by $1\frac{1}{4}$ in. thick, fitted with rubber gaskets and moistened with a 20% solution of caustic potash. The discs may be washed and recharged until the pores are blocked, when they can be replaced at a cost of about 25 cents.

Manufacture of Nitric Acid from Chili Saltpeter in Great Britain.¹ The following detailed method as taken from the general process employed at H. M. Explosives Works, Gretna and Dornock, may be regarded as representative during the period 1919. The process comprizes heating sodium nitrate with sulfuric acid in retorts by means of producer gas, the nitric acid being distilled off, condensed and collected, leaving a residue of niter cake which is ultimately run out of the retorts and collected.

Niter Storage Sheds comprize three stone-built buildings, each 212' by 75' wide by 24' high at the eaves, with concrete floor and corrugated iron roof, each shed having a working capacity of 5000 tons. Niter stocks are brought into the sheds by railway cars on elevated standard 4' 8 $\frac{1}{2}$ " rail gauge tracks (two to each shed), built on stone piers. The niter is dumped out of its containing bags on to the floor of the shed. Running along the floor of each shed are three sets of 18" gauge bogie track to provide a means of trucking the niter to the dryer and to the nitric acid retorts. The floors of the sheds are drained to small sumps, from where liquors can be recovered and transferred to the bag washing plant for recovery by evaporation.

Cummer Drier. Two driers are provided for drying the nitrate before use in the retort house, these driers being driven by 2 \times 20 H. P. motors. The wet niter is tipped into the house from an outside rail and shoveled into a hopper feeding two crushing rollers set one inch apart. These rollers crush the niter, which falls on to a small feed plate over which pass rotating arms which throw it into the boot of a bucket elevator; which delivers the wet niter into a Cummer drier. This drier consists of an inclined revolving cylinder fixed in the flue of a coke furnace. The wet nitrate is fed into the higher end, and owing to the inclination and rotary motion of the drier, is carried through the hot cylinder in a direction opposite to that of the hot gases. These

1. For this data and other information, the author is indebted to the courtesy of the British War Office and Mr. J. C. Burnham, Superintendent H. M. Factory, Gretna, Scotland.

hot gases from the furnace, after circulating round the drying cylinder, return through the cylinder to the outlet flue, carrying away vapor from the crude nitrate. A fan draws the gases from the drum and passes them to a steel chimney 3' in diameter and 40' high. The temperature of the niter leaving the drying chamber is about 60°. The dried niter is delivered from the drum to a bucket elevator, which lifts it to a storage bin having a capacity of 150 tons. Each drier is capable of drying 80 tons of niter from 2.5% H₂O to 0.5% H₂O per 24 hours, the fuel consumption (coke) being 0.014 long ton per ton of niter handled.

Cleaning of Drying Chamber. There is a tendency for the drum or drying chamber to become caked with hard niter, this being more pronounced in wet weather. The remedy is to run through, say once daily, 20 or 30 iron balls—eight-faced and pointed, which treatment usually removes the bulk of the scale.

Conveying Niter from Bin to Retorts. The bottom of the storage bin is fitted with six discharge chutes one foot square, which, when open, deliver the niter into bogies. Each bogie passes over a weigh-bridge and the contents are adjusted until 10 cwt. dry niter are in the wagon. This is then taken to the retort house and raised by means of an electric lift to the retorts charging platform.

Electric Lifts. Two electric elevators are provided, one at the end of each house. Each is driven by a 12 h. p. motor, and lifts a net load of 10 cwt. To avoid corrosion the electric controls are placed in a separate shed—out of the way of acid fumes.

Sulfuric Acid Storage. Two 9' × 30' boiler tanks, elevated on brick piers, are provided for this purpose. From these tanks the acid flows by gravity into the retort house and communicates with the sulfuric acid feed tanks, one of which is allotted to each retort.

• *Sulfuric Acid Measuring Tanks* are mild steel cylindrical tanks 53" deep and 51" diameter, and conveniently hold two tons of sulfuric acid. Each is provided with a lid, gauge glass and inlet and outlet valves. From experience it was decided that the gauge glass fittings are too small and the gauge glasses unreliable. All tanks are dipped before and after use, one inch acid being equal to 0.059 tons 92% S/A. The tank has a sloping

bottom to the outlet valve. Each tank is elevated and rests on brickwork standing 30" high. The whole rests on a leaden tray 6' \times 6' \times 2" with a one-inch diameter exit hole which connects to a lead launder 4" \times 4", and in turn connects to the drain. The outlet from the sulfuric acid measuring tanks is by a 2-inch lead pipe which connects to a permanent feed pipe fitted up to the retort lid. The feed pipe is of cast-iron and flanged to the lead delivery pipe from the tank. Connection into the retort is made by a "T" piece, provided with a blank flange for cleaning purposes.

Improved Type of Sulfuric Acid Measuring Tank. In order to eliminate the errors occurring in dipping these tanks, an improved tank was developed, the same tank being used. A hole was cut in the tank, about 4' 3" from the bottom and an overflow pipe inserted. Next an iron plunger was placed inside, connected with a pulley and chain to which was attached a pointer adjacent to a scale. When a tank was to be used it was filled up to overflowing, and, according to the strength of acid and nitrate content of the niter, the plunger inside the tank was adjusted by means of the screw. This gave a definite volume of acid for each charge of nitrate. This style of tank was found satisfactory, and when in use can be depended upon to produce niter cake of uniform acidity.

The Retorts and Settings. The retorts are built in each house in sets of three, the brickwork settings of these batteries being separated by passages 2' 9" wide. The retorts are gas-fired from the side nearest the condensers and tapped from the opposite side, so that these passages are useful as providing a way of communication for tappers who need to examine the fires, or for firemen who need to adjust the flue dampers. The retorts are completely enclosed in brickwork, excepting the man lid, which is used for charging the retort. Immediately behind the retorts, and about one foot above the brickwork top, is a steel plate charging platform carrying the bogie tracks from the lifts from which the cars of niter are conveyed to the retorts. The retort is of cast iron, consisting of a lower portion, cylindrical in shape, with a rounded bottom and a cylindrical extension ring 36" high, the two parts being made one by a rust joint. The lid is very slightly dome shaped, and fits into a collar in the

extension ring, connection being made by means of a rust joint. The lid has a large hole about 2' 8" diameter, to which is bolted, by means of fifteen 1-inch bolts, the iron casting which embodies the charging man-hole, which is closed by a man-lid, and the 8"-diameter circular hole into which is fitted the uptake to the condensing system. The total capacity of the retort is about $9\frac{1}{2}$ tons of water. This size has been found suitable for the decomposition of two tons of nitrate of soda.

Tapping Hole. At the lowest end of the retort is a 2-inch outlet for the niter cake. The outlet extends by a pipe to about one inch outside the brickwork setting. Round the end of the tapping pipe is fitted a collar which carries a screw-plug holding device to keep in position a cast iron plug used to close the hole, an acid-tight plug being first made of damp clay. The type of retort now being fitted has a different type of tapping hole, being 4" in diameter at the end, and instead of having a block of iron as plug, has a swing door, which is kept in position by means of a screw. This is a decided improvement on the old pattern.

Firing of Retorts. The retorts are gas-fired by producer gas, which is led from the main gas flue through a 4" pipe, controlled by a valve, to a horizontal passage 8" square beneath the retort. A large amount of tar condenses in this 8" passage, and at intervals is drawn off through a cleaning-up door. The gas then passes through a square hole into a firebrick combustion chamber, which is approximately 22" \times 48" \times 24" high. A large square firebrick is placed above the hole, supported on bricks, in order to spread out the flame and keep it from impinging on the retort too much, and also serving to distribute the heat more evenly.

The Flues. The products of combustion pass through the flue system, which consists of four horizontal circular flues approximately 15" deep by 9" broad, built round the retort, and so arranged that the gases must travel round the retort before passing to the next flue above. Each flue is provided with four explosion doors. From the topmost flue the gases descend to the waste gas flue leading to a 100-ft. steel chimney stack.

Condenser Platform consists, in each house, of an upper and lower deck, the upper deck serving to support the condensers and the fume main, and the lower deck to carry the acid mains. The receiver platform is built alongside the lower condenser deck,

and a little below it in level, so that the main can be set with a good fall in the direction of the flow. The condenser deck is built of wood or of steel and acid-resisting brickwork. The receiver platform is supported on acid-resisting brick piers.

The Condensing System. Uptake Pipe and Cascade. The uptake from the retort is of 8" Narki metal, and is carried up vertically about four feet before bending over to connect with the cascade, which slopes down at an angle of 80° with the vertical. The cascade is built of straight pipes. Cascades of Narki have been put in, also of Ceratherm, both being an improvement on pottery-ware.

The Condensers. The fume passes from the cascade through an 8" Kneebend into Woulffs bottles. The first bottle is of 40 gallons capacity; then through another 8" air condenser into a smaller bottle, 15 gallons capacity. From this bottle the fumes pass up into a breeches-piece into the first headers of the first two Hart condensers arranged in parallel. Each of these sets consists of 26 tubes 6' 6" long \times $1\frac{1}{4}$ " diameter. The tubes are sloping, so that any condensed acid runs back to the smaller of the two bottles above described. Any uncondensed fume passes from the top of the rear headers into a third Woulffs bottle of 10 gallons capacity, thence into a third Hart unit. This unit is differently constructed from the first two units. In this unit the gases are drawn up from the third bottle through one half of the tubes, which slope in the same way as the other two sets of tubes. Any acid condensing there falls back into the 10-gallon bottle, thence to the strong main. From the lower set of tubes (15) fumes pass to the upper set (11), which are sloping in the opposite direction. Any gases escaping condensation are drawn from a breeches-piece at the top of this third condenser standard, and travel into the fume main, which connects to the tower system. The first and second bottles are each provided with two 1" bib cocks, which serve to run off acid to the strong and weak mains respectively. All acid from third bottle runs into the strong main, as only strong acid is made in this header, when the charge is on reaction.

Condenser Tubes are covered by means of scouring cloth, which serves to distribute water evenly over the surface of the tubes. The cloth is torn up into strips 4" wide, and is interwoven

with the tubes, round the first tube to the right, thence to the second tube by the left, and so on down the standard. The cloth is kept from the standards about 4" to 6". Rubber rings $2\frac{1}{2}$ " diameter are used on the glass tubes at their lower end to keep water from the joints where the glass tubes enter the standards. The quantity of cloth required for a set of three standards is 300 sq. ft. About 2,000 gallons of water is run down a set of tubes per charge. The surface area of the glass condensing system (3 sets) is 159 sq. ft. The water from the condenser standards is collected in a trough 6' 6" \times 4" deep and 6" wide, from which it is run down to a common drain, fitted with a "V" notch. Samples are taken daily and analyzed. The average loss is 10 lbs. nitric acid per house per day.

In another section, the system of two Woulffs bottles which has been described above is replaced by a double-entry "S" bend. The gases are led from the cascade through a knee bend into the double-entry "S" bend, and pass up into the headers of the first two Hart units, arranged in parallel as before. All acid condensed in the two Hart units falls back into the "S" bend, and ultimately to the main, through a "still watcher." The escaped fume passes to the third header by a breeches-piece. The third set of tubes is identical with the first two. From the "still watcher" the acid may be led into either the weak or strong mains and collected.

Condenser Joints. As there are more than 150 joints connecting the condensing system of each retort, the greatest care is necessary in selecting jointing material. The glass tube is placed in position, and a ring of $\frac{1}{4}$ " blue asbestos cord put in. A layer of asbestos putty is then inserted, the same repeated, and the whole faced with a mixture of asbestos powder and silicate. When this is properly set the surface of the joint is painted over with bitumastic paint. These joints, if properly handled, will last a long time. Sudden pressures in the retort, and sudden rushes of gas must be avoided if such joints are required to have a long life.

Comparison of the Two Condensing Systems. The presence of the bottles and the peculiar construction of the third Hart unit have a throttling effect on the retort, and it is noticeable that "blows" are much more frequent and violent. However,

against this, condensation is more complete, and less tower acid is recovered. The presence of 1" bib cocks in Woulffs bottles has been the cause of considerable difficulty. In addition to causing loss of acid, destruction of woodwork, breaking of cocks, the bottles are a decided disadvantage over this double-entry "S" bend. Ultimately the bottles in the first described condensing set have been discarded and "S" bends substituted. This does away with leaky cocks, and is a decided improvement.

Acid Mains. The acid mains are 3" in diameter, and built of 2' to 2' 6" lengths of earthenware pipe. They run the entire length of the house, and are supported on brick arches on a platform below the condensers. Each condensing set delivers into the mains by branch pipes.

Strong Main. This connects with a 3" earthenware pipe which runs at the back of the strong receivers, and gives off branches to the three lead cooling coils. Each branch is closed by means of a 3" earthenware cock, and there are three more similar cocks along the main, behind the receivers, so that any particular section may be cut off for repair work without interfering with the running of the plant.

Weak Main. This is continued along the platform and outside the house to the weak receivers. Eight branch pipes with suitable earthenware cocks connect to the eight receivers, which are reserved for weak acid.

Lead Cooling Coils for Concentrated Acid. Three 2" lead coils are provided in each house, being immersed in iron tanks containing running water. The acid exit from each coil branches to two lead receivers, a 2" earthenware block cock being provided on each branch to enable the acid to be run to either or both receivers.

Concentrated Acid Receivers. These are built of 20-lb. lead in the shape of cylinders, 8' 3" diameter and 30" deep, each receiver having a capacity of about six tons of strong nitric acid. Six vertical iron "T" beams round the circumference and two encircling iron bands strengthen the receiver, and the top is supported by six lead-covered iron "T" shaped rails. A man-lid and a 4" dipping hole are provided in the top of each receiver, the former being permanently bolted on, while the latter is cov-

ered by a lid which fits into a lute containing a little vaseline. The outlets from the receivers are 2" earthenware cocks, which connect with a 4" lead main to the mixing station. Under each outlet cock is a lead drip tray, and these trays connect by an earthenware pipe to an earthenware blow egg. A 4" earthenware pipe connects each receiver to the fume main, and a lead pipe perforated on the upper side passes round the interior of each receiver, and serves for the introduction of compressed air to mix the acid before sampling.

Weak Acid Receivers. Ten receivers are provided for weak acid. Two of these are reserved exclusively for tower acid. They are of earthenware, of 100 gallons capacity, and of cylindrical shape. The lid is separate and jointed with the usual asbestos jointing. The acid is run by gravity through 1" earthenware pipe cocks into a 3" earthenware main to the mixing station. A 2" pipe connects each receiver to the fume main, and there is a dipping hole, closed by an earthenware cover, in each lid. The receivers stand upon a flooring of acid-resisting tiles. Any drips from the cocks are collected in an earthenware pipe placed underneath and led to a carboy located underneath the stage.

Fume Main. The exit from the third Hart unit of each condenser set is connected to a large 8" earthenware fume main which passes along each house. A main of the same size branches off to the absorption towers from the middle of each house. To the first main is connected a smaller 6" main which serves to exhaust the receivers by means of the 4" and 2" branches above described. The fume main is built on a slight slope so that any condensed acid runs to the lowest point, where it is drawn off to the receivers through a suitable 2" pipe.

Drip Recovery Eggs. Two earthenware eggs, each of 77 gallons capacity, are installed beneath the strong receiver platform, one in each house. Drip pipes and runs from all parts of the house, drip trays, and earthenware jugs are all emptied into these eggs. Any acid spilled from cracked mains, and acid collected in carboys, is put into these eggs, and the contents blown to the receivers by compressed air at 10 lbs. pressure. The acid is delivered through a 2" earthenware line, to either strong or weak receivers as required. The inlet cock is of earthenware and the air pipe of lead. Connections are made by means of flanged

joints packed with asbestos and compressed with iron clamps.

Absorption Towers. The 8" earthenware mains already described above are carried outside the houses on wood trestles to the absorption towers, there being two sets, each of eight towers, one set being connected to each house. The towers are elevated on brick piers 12' high, and both deal with the uncondensed gases from the houses. The towers are built of stoneware, and are constructed in five sections, each section being 3' long \times 3' diameter. The column of five sections rests on an earthenware saucer 9" deep and having an internal diameter of 3' 6". The bottom section has a 9" take-off to connect the gas inlet to the fume main. The towers are themselves packed with graded quartz, which rests on a tiled archway built in the saucer to give easy access for the fumes. The size of the quartz packing varies from 6" stuff at the bottom to 2" stuff at the top. At each section of the joints a 2" perforated plate is provided with 1" holes. The saucer at the foot of the tower is fitted with a 1" cock, which delivers the weak acid into a constant level receiver situated just below. At the top of each tower is an earthenware acid-distributing bottle known as a "bee-hive," fitted with four $\frac{3}{4}$ " bib cocks. Two of these are connected to deliver acid from the beehive down the tower. The other two are provided so that acid may be forwarded from one tower to another through 1" glass pipes.

Constant Level Receivers, already mentioned, are made of earthenware and measure 27" internal diameter. They hold acid to a depth of 20", at which level each is connected with the next in the series by means of a $1\frac{1}{4}$ " glass tube, which maintains a constant level in all receivers.

Pohle Air Lifts or Acid Elevators are used for lifting the absorption acid from the constant level receivers to the tops of the towers. The gases conveyed along the fume main enter at the foot of No. 1 tower are drawn through the tower, leave by an 8" "U" bend, and are conveyed to the bottom of the second tower, and so on through the series. The absorption is carried out by counter circulation of absorbing liquid (water or weak nitric acid), and the nitrous fumes. A constant supply of acid to the well is received from the constant level receivers. Air at 15 lbs. per sq. in. is supplied via the glass air tube, and a con-

tinuous but jerky lift of acid to the beehive on top of the tower is maintained.

Compressed Air required for operating the "Pohles" is carried to the tower along a 2" branch pipe from the main air service at 80 lbs. per sq. in., and is reduced before it is used at the towers to 15 lbs. per sq. in. It is connected to the individual lifts by means of stout rubber connections taken from a 1" pipe. The compressed air serves two purposes, viz., to elevate the acid from bottom to top of the tower, and also to oxidize the NO passing through the towers to NO₂, which in contact with H₂O forms HNO₃.

Campbell Ejector. A 30" diameter Sirocco fan, driven by a 10 h. p. British Thomson Houston motor, causes a blast of air to be driven through an earthenware injector. The suction pipe, also of earthenware, communicates with the gas outlet from No. 8 tower. By this means a vacuum of 6" water gauge is produced on No. 8 tower. This falls away to 2" on No. 1 tower, and to 1/8" to 1/4" at the retort head. The ejector is perfectly simple, and causes no trouble. The fan delivers at a pressure of 6" water gauge at the rate of 40 cubic feet per second through a 9" pipe.

Niter Cake Disposal. Tapping Side of Retort House. This extends the full length of the house. The floor is built of acid-proof bricks laid on a concrete bed, the joints having been run with molten sulfur. The floor is easily cleaned and very resistant to acid. Each retort is provided with an iron chute 9' long, 1' wide, and 1' deep, the top end of which rests in the recess of the retort wall, around the tapping hole, and the lower end fits into a wooden extension chute of similar dimensions, except that it is about 12' long. A wooden trestle supports the whole. The lower end of the wooden chute rests over a lead-lined drain 12" deep × 18" wide. This launder runs the whole length of the retort house. Each retort is provided with 2" water valve, situate at the junction of the water and wooden chute. This conveys a copious supply of water to dissolve the niter cake, down the wooden chute, and into the gutter, whence it ultimately runs into the river. This process has been abandoned, and all the niter cake is recovered in a granular or lump form.

Niter Cake Granulating Station. A portion of the niter cake is recovered in granular form by directing the molten mass along

the chute to a point where it falls and is met by a powerful blast of compressed air from a 2" horizontal iron pipe, with a slit 4" long, adjustable in width from $\frac{1}{50}$ th of an inch to a $\frac{1}{16}$ th of an inch. The molten cake is immediately solidified and falls like fine snow on the floor, roof and sides of the blowing house, which is 40' long, 15' wide, and 12' high. The material is in fine granular form, and finds a ready market, being usually put up in 40-gallon casks. The present system of recovery is as follows: The iron chutes from four retorts each connect with another chute running at right angles. From one end of this latter chute another one projects downward to the point where the molten cake, after falling 13", meets the blast of air from the horizontal pipe at an angle of about 45°. The four adjacent retort chutes are similarly fitted. These two iron chutes terminate at the entrance of the blowing shed, and each chute is provided with a blower to itself. The pressure of air at this 2" pipe is 80 lbs. per sq. in., and a gauge is placed near by. When the pressure falls the cake is not properly granulated. The house to which the granulated cake is blown is built up of old galvanized sheeting, the floor being laid with acid-proof bricks laid in cement, and jointed with asphalt.

Sliter Cake Recover Pans. The whole of the north house is provided with pans, four to each retort, size 12' \times 5' \times 8". These pans rest on brickwork, and are raised some three feet from the ground. A railway track passes along the line of pans, the full length of the house. The charge of molten cake is run evenly into the four pans, allowed to solidify, and then broken up with a hammer and thrown into the cars alongside.

Tapping Floor of North Retort House. The differences worthy of mention from the description of south house tapping floor are:

(1) Floor constructed of concrete, which does not resist the action of acid as well as the acid-proof bricks.

(2) A half-round earthenware drain takes the place of the leaden launder in the south house.

Water Supply. This is similarly arranged in both houses. A 4" main in each house, fitted with a main stop valve, supplies water to the Hart condensers. The outer 4" main with stop valve supplies water to the tapping chutes. This main completes a circuit round the house, branches being taken off at inter-

vals: (1) For tapping retorts. (2) For 1" hose pipe connections. (3) For cooling worms for strong receivers, etc.

With a view to effecting economies in the water consumption on the plant, large galvanized tanks have been placed on girders about 15' from the ground in both houses. These tanks receive waste water from the acid mixers coils, which previously was lost, each tank holding 1,000 gallons water. The outlet pipe from the tank connects the 2" main supplying the water for tapping the retorts, and by means of a ball valve arrangement (similar to an ordinary cistern), a plentiful supply of water can always be depended upon, either from the mixers overflow or from the main.

Joints—Nitric Acid Work. The present method of jointing earthenware socket pipes, etc., for both liquid and fume is as follows:

A ring of blue asbestos cord of suitable thickness is first placed in the joint, then the socket filled with grease packing almost to the top of the socket, and the joint finished off by pointing with silicate packing. Where the socket is sufficiently deep, two rings of asbestos cord are put in with a layer of grease packing between each.

The men employed luting socket pipes are very apt to hammer in thick cord with the idea of getting a tighter joint, but this should be prohibited, as the cord swells and the socket is split. This applies more particularly to pipes, etc., made of special material, e. g., ceratherm. Glass tube joints on Hart condensers are made in a similar manner, but in each case two rings of cord must be used in order to make a tight joint.

On some plants the chemists in charge prefer the joints to be tarred when finished, others prefer painting with weak nitric acid, but if water can be kept away from the joint (and it ought to be), painting with a fairly strong solution of silicate of soda puts a fine, hard finish on the joint, and prevents the jointing material cracking. Painting with nitric acid helps the joint to harden quickly, but it may do more harm than good to the luting.

Labor Requirements. For two adjoining retort houses, each containing 24 retorts: The plant itself is almost entirely operated by male labor. The handling of niter, however, is done by girl labor. The receivers for storing the nitric acid and the

issuing of this to the mixers is also done primarily by girl labor.

Female Labor. Nitrate of Soda Handling. Sixteen girls per shift are engaged as under: 1 charge hand; 3 girls picking down niter; 6 girls filling bogies and conveying same to the drier; 3 girls feeding driers, (1 spare); 2 girls conveying niter from dry bins to hoists; 1 girl checking weights of dry niter.

In addition to the above girl truckers, two dip or receiver girls per shift are employed as process workers.

Total female labor per shift, 18 per house; total for day, 54 girls.

Male Labor. 1 foreman per shift; 21 operatives per shift.

The various process operatives are all classified, and the men carefully selected for their respective jobs. The senior process man is the reaction man. He is responsible for a series of 12 retorts and his duties consists of:

- (1) Running the charge of sulfuric acid into the retort.
- (2) Controlling the distillation.
- (3) Attending to gravities of the nitric acid.
- (4) Seeing that his section is kept clean and tidy.
- (5) Controlling condensers (cloths and water), not the replacing of broken tubes.

Tapping Retorts. Two men are provided in each house for this, their work being to empty the retort of its niter cake, when instructions have been given for this to be done. The cake as already described, falls into pans to be recovered. They are responsible for all plugs being properly secured before the acid is run in to the retort.

Charging Men, of which two are provided. Their work consists of bringing the niter along to the retort mouth, emptying same into the retort, cementing up the lid, and generally cleaning up the retort top.

Condenser Men. Two men are engaged attending to condensers generally. Replacing broken tubes and patching and overhauling condenser standards and joints.

Granulating Cake. Two men per shift required for this.

Cummer Drier. One man per shift required for these driers, who also attends to the tarring and greasing of all bogies.

Lump Cake. Three men engaged on the removal of lump cake to the wagons which run alongside the pans. One senior

charge hand is usually provided for each separate shift of labor.

Summary of Male Process Labor. 1 senior charge hand; 4 reaction men; 4 tappers, 4 charging men; 1 man in charge of Cummer drier; 5 men disposal of niter cake, 2 condenser men, total, 21 men per shift. The foreman is generally responsible for the running of the plant and control of the labor.

Maintenance of Labor. The wear and tear on a plant of this kind is naturally great. A gang of earthenware pipe jointers is engaged on the nitric acid sub-section. They are not attached to any particular plant, but may be called upon when required. Fitters are also available for engineering troubles, as also plumbers, but none are permanently on the retorts staff.

Attached Labor. The fires are controlled, under the orders of the reaction man, by a man supplied by the producers plant. Two firemen per shift are provided for the two retort houses. Another man belonging to the acids mixing station supplies the sulfuric acid for the two retort houses.

Plant Operation. Sampling of Niter. The crude niter is sampled weekly. When sampling, about 20 cwts. are generally taken down, halved and quartered in the usual way until 28 lbs. are obtained. This is then submitted to the laboratory. The following is an average analysis of the sodium nitrate:

| | | |
|---|--------|-----------------------------|
| NaNO ₃ | 95.85% | } = NaNO ₃ 96.6% |
| KNO ₃ | 0.98% | |
| KClO ₄ | 0.14% | |
| NaCl, Na ₂ SO ₄ | 0.50% | |
| Insoluble..... | 0.06% | |
| Moisture..... | 2.20% | |
| Iodates..... | Trace | |

This is customarily dried so that the finished sample contains 0.5% moisture, this usually bringing the nitrate content of the sample to 98%.

Usage of Sulfuric Acid. In each retort two tons of niter are distilled with approximately two tons 92% sulfuric acid. The following are the actual figures:

$$\begin{aligned}
 2 \text{ tons niter @ } 98\% &= 1.96 \text{ tons pure NaNO}_3 \\
 1'' \text{ dip in tank} &= 0.059 \text{ ton.} \\
 34.6'' \text{ used} &= 34.5 \times 0.059 \times 2.035 = 92\% \\
 &\quad 1.872 \text{ H}_2\text{SO}_4 \text{ (2 tons C. O. V.} \\
 &\quad \text{of 92\%)}
 \end{aligned}$$

Ratio of sulfuric acid to nitrate in terms of pure chemicals:

$$= \frac{\text{H}_2\text{SO}_4}{\text{NaNO}_3} = \frac{1.872}{1.960} = \frac{0.956}{1.000}$$

Firing the Retort and Gas Consumption. The above materials are put into the retorts, the lid luted down with cement, and the gas fire lighted. The damper is adjusted at the back of the flue, and the air ports in the front, to give complete combustion of the fuel. The following are average producer gas and waste flue gas analyses:

| Producer Gas | | Waste Fuel Gas | |
|-----------------------|-------|-----------------------|-------|
| CO ₂ | 4.0 | CO ₂ | 8.1 |
| CO..... | 28.0 | O ₂ | 9.9 |
| H ₂ | 11.1 | N ₂ | 82.0 |
| CH ₄ | 1.4 | | |
| N ₂ | 55.5 | | 100.0 |
| | 100.0 | | |

In order to determine the exact gas consumption a rotary meter is affixed to each retort. Experiments were made under varying conditions, to determine exactly the coal consumption. The average figure recorded was 30,000 cu. ft. reduced to normal temperature, for a charge of two tons niter, which gives 1.43 tons HNO₃.

1 ton coal gives 130,000 cubic feet gas.
 (1.43) 1 charge uses 30,000 cubic feet gas.
 Hence 1 ton uses 20,000 cubic feet gas.
 equivalent to 0.14 ton fuel per ton HNO₃.

The Distillation. When a retort is tapped, the charging lid is removed and the retort dipped to make sure it is tapped clean. It is a rule on the plant that the tapping hole must be plugged before the soda is charged; this is done to avoid the possibility of the acid being run in before plugging.

The soda charge of two tons is weighed in four bogies, ten cwts. each, and is charged into the retort by means of a portable chute. After tipping, the bogies are swept clean, and any soda spilt is swept up and added to the soda in the retort. The charging chute is now removed. The seat for the lid is covered with clay, the charging lid put on, and cemented down with ordinary cement. In running in the acid by the first method the center plug is left out, but in the second method the plug is luted down with clay and cement.

• Meanwhile the charge of sulfuric acid, 2.05 tons of 92% acid,

or 2.01 tons 93%, is measured in the kettle. There are two methods of running in the acid. In the first method a temporary connection is made from the kettle to the retort, using a short piece of iron pipe, which dips into the acid charging hole in the lid. In the second method a permanent connection from the kettle to the retort is used, which is independent of the charging lid. A cast-iron tee-piece is bolted to the retort cover, and is connected to the pipe from the kettle by a 2" iron pipe with a "U" bend to minimize the effects of a blow-back while charging. The tee-piece on the retort is necessary on account of the fact that the acid inlet must be cleaned after practically every charge.

After the acid has been added and the plug luted down, the fire is started, unless the retort be very hot, in which case it is advisable to wait a short time. Sufficient fire will be put on to make distillation commence in about one hour. If the retort be cold much longer will be required—up to three or four hours.

For ordinary running a 14 to 16 hour cycle is the most usual, with a distillation time of 12 to 14 hours. As soon as a retort is warm, a few brown fumes appear in the condenser tubes. A clear indication of the commencement of distillation is given by a rapid rise in the uptake temperature to 90°. When the pot temperature has reached 90°–100° the temperature will steadily rise for the next two or two and a half hours, with a regular evolution of nitric acid vapors.

As soon as the "pot" reaches a temperature of 115°–120° the reaction between the sodium nitrate and the sulfuric acid becomes violent. The pressure in the retort rises, and the manometer on the retort head gives indication of this. At this time it is usual to have the fire out while this violent reaction is in progress to avoid damage to the pottery. This reaction lasts from 5–20 minutes, depending largely on the speed with which the pot temperature has been raised. This period is very clearly shown in the condensers. Before it occurs the retort distils regularly and the gases in condensers are brown, but during this period the vapors in the condensers are colorless, or almost so. As soon as this violent stage of the reaction is over the tubes quickly become colored again, and the fire is started.

During the height of the reaction the pressure in the cascade is shown as 3"–4" water pressure by the manometer. Whenever

the manometer shows less than one inch pressure it is safe to re-light the fire. For the next four or five hours the rate of distillation drops off, the uptake temperature will drop somewhat, from 135° to 130°, and the fire must be materially increased.

From now onwards the sp. gr. of the liquid distilling is taken every hour by the "reaction man." When the sp. gr. of the distillate falls to 1.465 the acid made is run to the weak acid receivers; till this point it has been running into the strong receivers. The distillation is now steadily continued till the sp. gr. of the distillate reaches 1.340; then the fire is extinguished, and the retort is ready for tapping. A retort is not actually ready at 1.340, but there is sufficient heat in the charge to finish the distillation while preparations are made for tapping. The end point is also shown in the condensers, because very little distillate is coming over. The uptake temperature drops considerably towards the end.

The term "Cycle" means the time a retort is charged until it is empty. "Dead time" means the length of time between the pot being empty and again charged. The cycle aimed for here is one of from 14-15 hours, which generally means a distillation period of 10-11 hours. "Blows" are very uncommon with the above times. With a lower cycle, say 10-11 hours, in addition to breakage of earthenware, there is increased decomposition of the nitric acid in the retort, which has been proved by the analysis of the gases in the fume main. Generally speaking, quick cycles do not pay. Longer cycles than 14-15 hours are not desired, as coal consumption increases and a larger quantity of nitrous acid is found in the distillate.

Tapping. The tapping of the retort has already been described. Great care is necessary to see that the tapping hole is kept clean.

When a retort is tapped two samples are taken of about 7 lbs. weight, which are sent to the laboratory, and an analysis made for sulfuric and nitric acid content. An average figure is as follows:

28%-29% total acidity as H_2SO_4 ; 0.06% HNO_3

The acidity of the sample depends somewhat on the stage of the tapping, and samples taken at intervals during a tapping gave results averaging 28.8% H_2SO_4 .

Condensation. During the process of distillation, the bulk

of the acid is condensed in the first two headers of Hart tubes. A small quantity condenses in the third set of tubes, and this usually contains upwards of 5% nitrous acid. Uncondensed gases pass to the fume main and to the absorption towers. For efficient condensation there must be provided both a large cooling surface and free passage for the gases without restriction of any kind, otherwise the gases will pass through and escape condensation in the one case, or a "choke" will develop in the other.

It is necessary for proper working to have a good vacuum on the plant. If a retort is not in use the damper is put in the fume pipe so as to avoid any unnecessary air getting into the system. It is found that for efficient condensation, a quantity of 1500 gallons should be passed over the condensers. This represents per ton of nitric acid produced a consumption of 1000 gallons. Careful experiments have been carried out to see to what extent the loss is in nitric acid from condenser joints. Twenty distillations were carried out in one retort. At the end of the twenty-first the water was only very slightly acid. The water was collected from each running, and up to the tenth one no acidity was shown.

Absorption. Cold water is fed into No. 8 tower (one nearest exhaust), and the $\frac{3}{4}$ " cocks on the beehive so adjusted as to give a progressive movement of acid through the system. Acid of between 60% and 65% strength is run off at No. 1 tower through a still watcher, in which a hydrometer is placed, so that the strength of the acid produced may be readily observed. The acid run off from the towers is conveyed to the storage by means of a 2" pipe.

Analysis of Acids Made. When a receiver is filled with acid, either weak or strong, a sample is taken and submitted for analysis. The analysis is returned showing nitric and nitrous contents and sp. gr. Before the sample is taken in case of the strong, the compressed air agitation is turned on so as to obtain a uniform sample. The average strength of the strong acid is in the neighborhood of 92.5%, with a nitrous content of 0.5%. The weak acid is of average strength 65%–68% HNO_3 . Nitrous content almost nil. The acid recovered from the towers is usually 50%–60% HNO_2 and the nitrous content 0.1%.

Capacity of Plant. Assuming 12 hours as the lowest cycle,

consistent with efficient condensation and few breakages, we have 1.40 tons HNO_3 from a charge in 12 hours. Allowing two hours dead time, the balance of the working day of 24 hours will give 1.16 tons nitric acid.

1.4 plus 1.16 = 2.56 tons HNO_3 per retort per 24 hours.

Each house contains 24 units, two of which are generally being repaired, we have—

$24.2 = 22 \times 2 = 44 \times 2.56 = 115$ tons HNO_3 per day.

Working Results. Underneath is an extract from February's 1918 report, which shows in detail the working results. The efficiency of the plant lies between 96% and 97%. The quantity of H_2SO_4 used per ton HNO_3 produced is about 1.35 tons.

The quantity of NaNO_3 used per ton HNO_3 produced is about 1.39 tons.

The following is an average percentage return:

Recovered as strong acid..... 87.2, strength = 92.5% HNO_3
 Recovered as weak acid (ex towers) 10.4, strength = 63.5% HNO_3
 Recovered as tower acid weak..... 2.4, strength = 56.5% HNO_3

Nitric Acid Retorts (North and South Houses).

Monthly Report.

Five weeks ended 7.30 a.m. 2nd Mar. 1918.

All weights in tons of 2240 lbs.

Total number of retorts charged — 138 $\frac{1}{4}$ wet; 1359 $\frac{1}{4}$ dry = 1498.

Total number of retorts tapped — 1505.

Sodium Nitrate.

| | | |
|-----------------|--------------|---|
| | | Charged |
| Amount wet..... | 276.5 tons. | NaNO_3 96.6% HNO_3 197.97 tons. |
| Amount dry..... | 2719.5 tons. | NaNO_3 98.41% HNO_3 1983.58 tons. |

Sulfuric Acid.

| | | |
|-------------------------|---------------|---|
| Amount..... | 3095.52 tons. | H_2SO_4 92.0% H_2SO_4 2849.44 tons. |
| Coal used in producers, | 401.54 tons. | |

Nitric Acid Produced.

| | | |
|------------------|---------------|--|
| Amount strong... | 1986.07 tons. | TNA as HNO_3 92.4% TNA as HNO_3 1835.62 tons. |
| Amount weak.... | 380.19 tons. | TNA as HNO_3 63.75% TNA as HNO_3 242.38 tons. |
| Ex towers..... | 106.67 tons. | TNA as HNO_3 59.7% TNA as HNO_3 63.67 tons. |

2472.93 tons.

Total 2141.67 tons.

Nitric Acid.

Lost.

Total TNA as HNO_3 charged to Plant as NaNO_3 2181.55 tons.

Total TNA as HNO_3 recovered..... 2141.67 tons.

Unaccounted for at mixers..... 20.71 tons.

Total amount lost..... 60.59 tons. (2.78%)

Physical Data.

Time of distillation, 11 hours 43 minutes.

Time of cycle, 14 hours 48 minutes.

Niter Cake. Composition as determined by laboratory analyses.

Percentage free H_2SO_4 ; 28.43% by analysis; 31.45% by calculation.

Fuel.

Coal used per ton of acid recovered..... 0.16 ton.
Coal used per ton of HNO_3 0.19 ton.

Nitric Acid.

Average strength of acid recovered..... 86.6%
Tons produced per retort..... 1.6%
Percentage recovered as strong acid..... 85.7%
Percentage recovered as weak acid..... 11.3%
Percentage of weak acid recovered in towers..... 3.0%
Total recovery: 97.22%

Nitric Acid Manufacture at Queen's Ferry Plant. From the excellent and exhaustive report of V. Gloag and J. Riley, the following data is reproduced:

Nitric Acid Plant: 1. *Niter Stores.* There are two stores, each 180' by 80' with a total capacity of approximately 8000 tons. The nitrate of soda is delivered to the factory, bagged in trucks, and is discharged into the stores direct from the trucks, which run along overhead gantries. There are two of these, running the whole length of the store. The empty bags are taken away immediately to the bag washing plant to be washed and dried. The soda is delivered from stores to Cummer driers in buckets, holding about 1 ton each, suspended from an overhead runway. There are three of these per store, so that any part of either store can be drawn from at will. The buckets are filled and delivered to the Cummer driers by female labor. Unfortunately at Queen's factory the soda sheds are 1.7' below the Cummer drier levels. This has materially increased the cost of handling. But the levels are now being adjusted.

2. *Cummer Driers.* Two driers in operation with approximately a capacity of 3.5 tons wet soda per hour. This has a moisture content of 2.5% (about) and is fed through an iron grid, where the lumps are broken up by female labor feeding the machine. The rate of feed is regulated to some extent by the revolving steel blade pushing the niter into the elevator, but is mainly dependent on the operative. A roller feed was installed on one of the driers but was not a success owing to the fact that the rollers were too widely opened, and were not adjustable. This type of feed if improved would be the best, as it would ensure an absolutely steady feed of niter of uniform size. The nitrate from the feed hopper is elevated to the Cummer driers by means

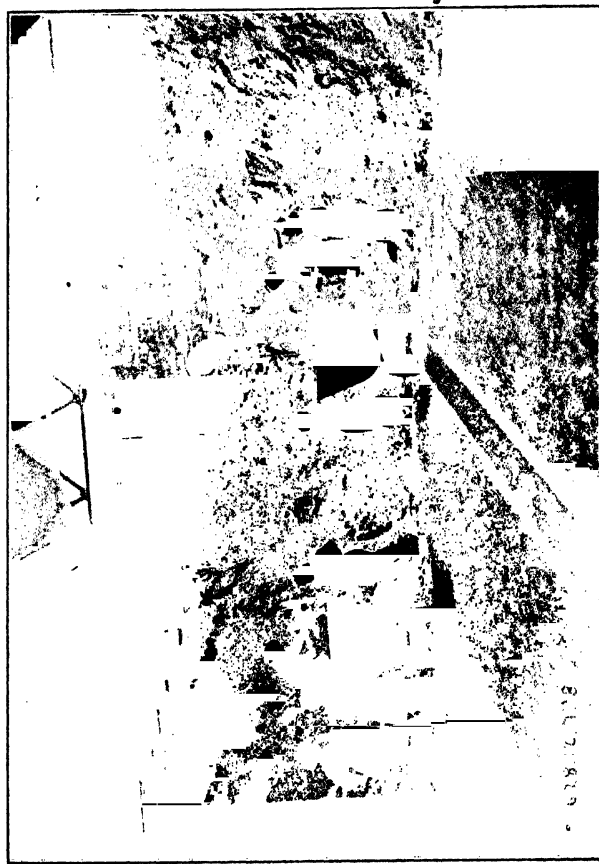


FIG. 46.—NITER STORAGE HOUSE (H. M. EXPLOSIVES FACTORY, GRETTA)

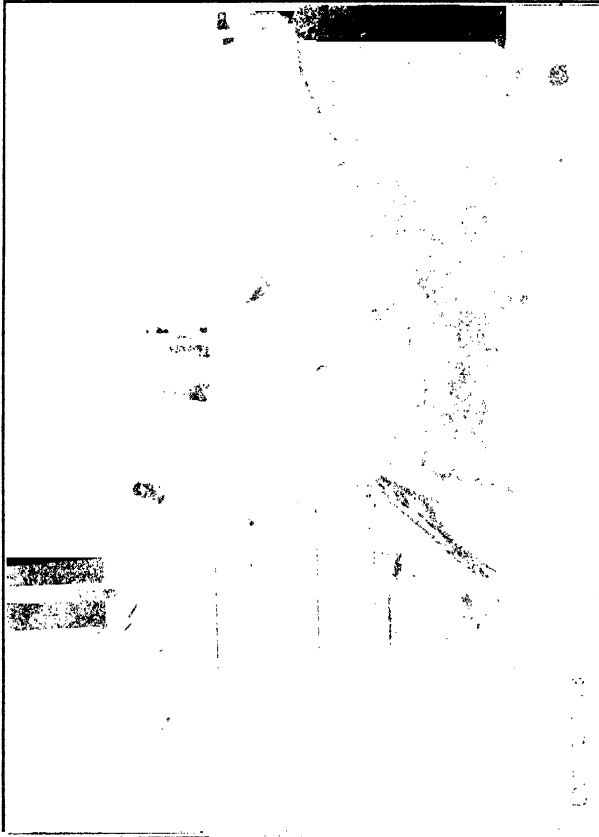


FIG. 47.—LOADING NITER INTO NITRIC RETORT (H. M. EXPLOSIVES FACTORY, GREINA)

of a bucket elevator and delivers into a chute, which feeds the revolving drum of the drier. The drum is $4\frac{1}{2}'$ diam. by 27' long, with a fall of 3.8" per ft. towards the delivery end. It revolves at 7 r. p. m., being driven by a 7 h. p. motor at 990 r. p. m. The niter is dried during its passage through the drum by means of hot gases from the fire box which pass first round the outside of the drum and then through the drum to the stack, the necessary draught being developed by a fan driven from the main shafting at 720 r. p. m. The original fire box was an automatic stoker, of American design, but owing to difficulties in obtaining spare parts, an ordinary fire grate has been installed to replace it. The fuel consumption is at present 0.3 ton coke per ton moisture evaporated. The dried niter is delivered from the end of the drum into an elevator which, in turn, delivers into a storage bin. There is one bin for each drier with a capacity of 60 tons, so that the total storage capacity is 120 tons. This was originally 40 tons greater, but when the retort capacity was increased by fitting of extension rings, the outlets from the bins had to be raised, which left 20 tons dead space per bin. The capacity of the drier properly operated is 3.5 tons per hour, or say on 22 hours' continuous working, 77 tons per drier per day. If operated with care the dried niter has a moisture content of 0.1% to 0.15%. Everything depends, however, upon uniformity in feeding, which could be guaranteed by a well-designed automatic feeder. The dried niter is conveyed to the retorts in buckets, suspended from an overhead runway, which passes over a weighbridge, to the lift, driven by an 11 h. p. motor, which elevates it to the charging platform.

3. *Retorts.* There are 42 retorts, divided into two houses of 21 each. For convenience in working each house is divided into 3 sections, each of which is served by a separate strong acid main, which delivers through a cooler to either one of the two lead storage tanks. In the general arrangement, the connections are so designed that in case of emergency, the acid from any set of retorts can be diverted to any one of the three mains. In this way any section of the acid main could be disconnected for repair without necessitating closing down the retorts ordinarily running on that main. In operating the plant, the retort is charged with 2.5 tons dried niter (98% to 98.5% NaNO_3) by

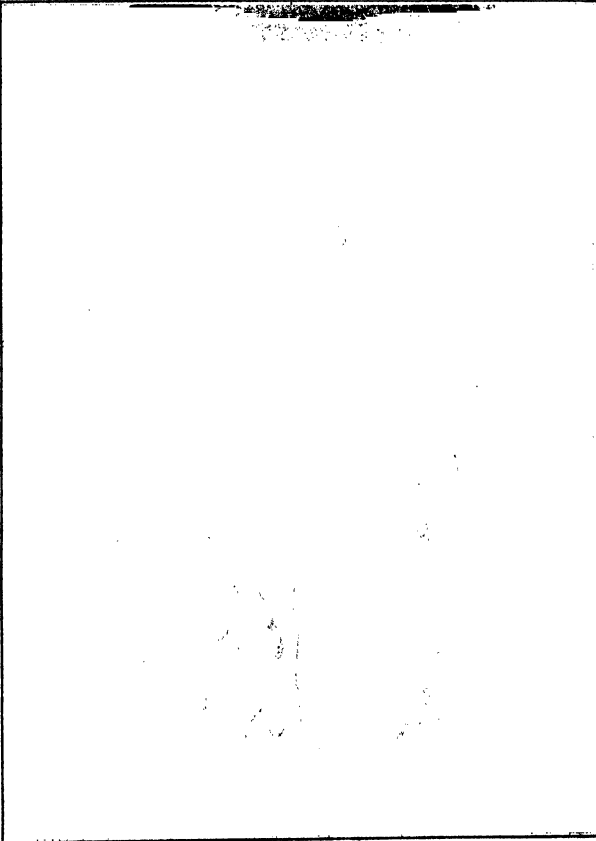


FIG. 48.—NITRIC ACID MANUFACTURE (H. M. EXPLOSIVES PLANT, GRETNA)

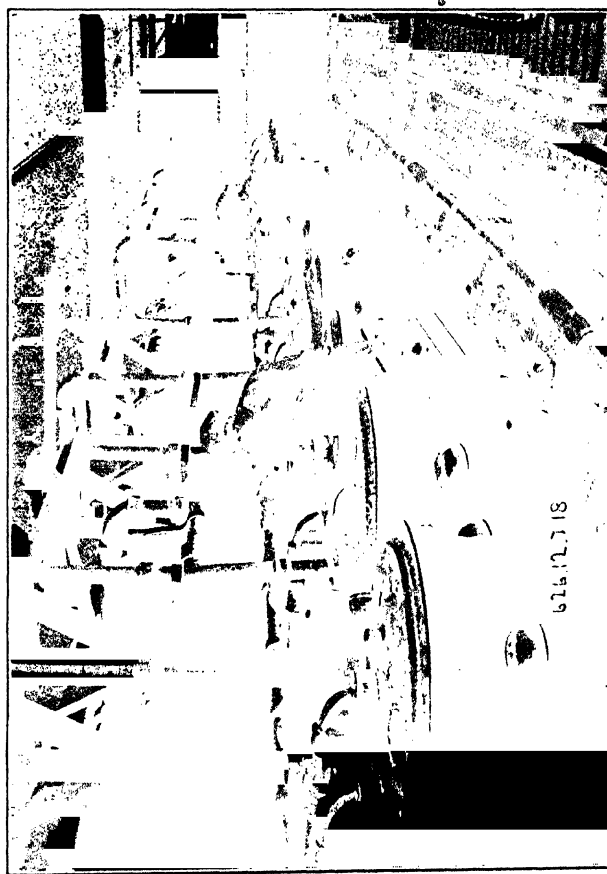


FIG. 49.—NITRIC ACID MANUFACTURE (H. M. EXPLOSIVES PLANT, GREYNA)

means of a chute, and after sealing the lid with ordinary clay, the requisite quantity of 92.5%-93.5% sulfuric acid is run through an ironac seal-pot, or through a hole in the retort lid. The acid is run down from a steel measuring tank 4½' diam. and 4' high. There are two steel storage tanks 8' in diam. and 30' long, which supply the feed acid to the measuring tanks in each house. The acid is supplied to these from the retorts feed acid mixing plant, or direct from the Gaillards, when the concentrated acid is of suitable strength.

The ratio $\frac{\text{H}_2\text{SO}_4}{\text{NaNO}_3}$ in the charge to the retorts aimed at is 0.95 NaNO₃ with a niter cake of 28% acidity. At present it is necessary to raise this to 0.97 if for any reason the retorts have to be worked more intensively than usual.

4. *Condensers.* In the main the construction of the condensing plant is as originally designed, the principal modification being the substitution of Narki metal for pottery. All the 8" cascade pipes from retort to condensers have been replaced by straight spigot and socket Narki 8" pipes. This metal has thoroughly justified its insertion, and replacements have been practically nil, the only maintenance required being periodical rejoining. Another part of the condenser replaced by Narki is the S or foot pipe from which the two headers for the Hart condensers rise. Condensers are of the usual Hart type, having two parallel banks of 26-1¼" × 6' 7" glass tubes, each leading into a third bank of 26 tubes of the same dimensions. The headers are 6" pottery ware and in nitric acid manufacture has proved most satisfactory. It must be remembered that the jointing of the tubes into the pottery header needs special care. Joints are made with two rings of blue asbestos cord and soft blue asbestos putty, faced with hard putty of silicate of soda, and asbestos powder, and finally waterproofed by painting over thickly with tar. The water is prevented from running into the joints by rubber rings placed around the tubes at a distance of about 1" from the end.

The operation of the condensers has required a great deal of attention. The sediment in the river water used for cooling purposes continually blocked the aluminium sprinklers initially installed, and these have now been replaced by wooden distributing launders. The tubes are draped with ordinary cheesecloth

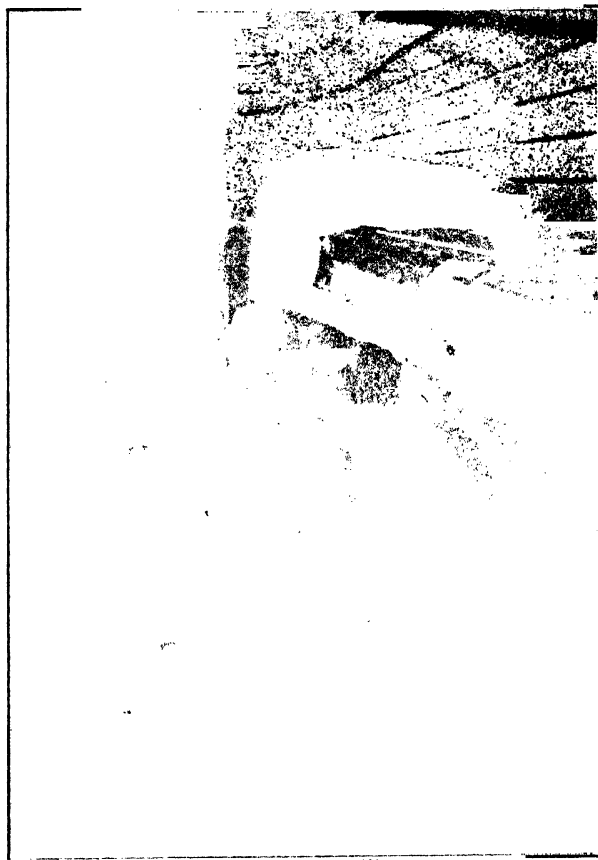


FIG. 50.— HNO_3 MANUFACTURE (H. M. EXPLOSIVES FACTORY, GRENA)

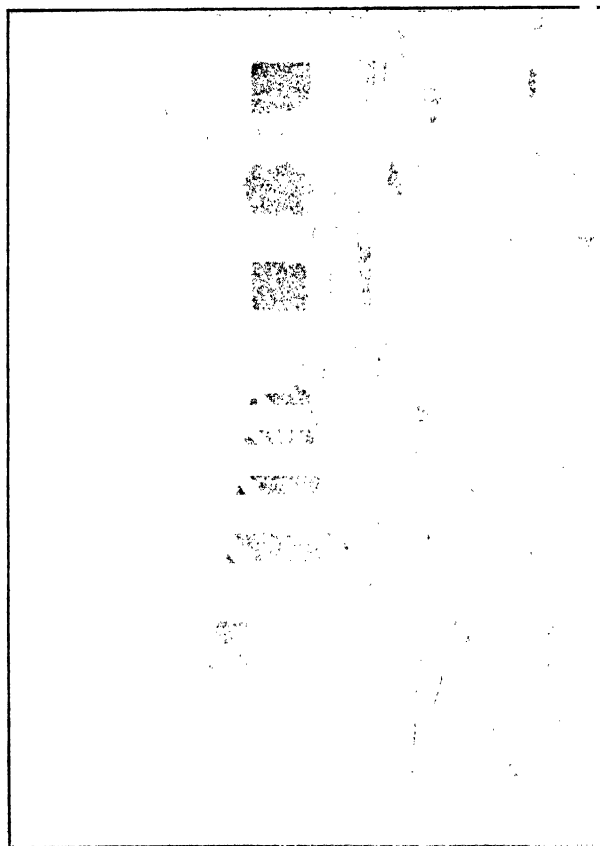


FIG. 51. --HNO_3 MANUFACTURE (H. M. EXPLOSIVES FACTORY, GRETTNA)

with serrated edges, and with reasonable attention an excellent distribution of water is obtained. On account of the dirtiness of the river water, the maintenance of the cheesecloth is no small matter, two girls per house being kept continuously at work, one day shift cutting and replacing this cloth, which requires removal every fortnight or so. The condensed nitric acid, containing 96% of the total HNO_3 recovered in the plant, runs off through the foot pipe to a glass domed still watcher and the 3" lead main. The run-off pipes and still watchers were originally supported by wood work, this has now been replaced by brick-work and broken pottery, which has proved more satisfactory.

5. *Absorbers.* The gases from the condensers pass into a fume main, which is 9" diam. at each end of the house, increasing to 15" at the center, where from a 'T-piece 15" main carries the gases to the absorbing towers—8 to each house. These are of the same type as those subsequently to be described on the denitrators. Water is fed into No. 8 tower and 55% nitric acid drawn off from No. 1 tower to the weak acid receivers, the circulation of acid over the towers being carried out by Pohle air lifts. The necessary draught for the operation of retorting is generated by a pottery ejector working on the induced draught principle, as described in detail in the case of the fans on the denitration plant.

6. *Coolers.* The nitric acid collected in the condensing system passes from the lead mains through a coil of $2\frac{1}{2}$ " lead pipe, made up of 7 coils 2' in diam. wholly immersed in water in a mild steel tank 3' in diam. and 3' deep. It is run into lead receivers, from which it is issued to the mixing plant. For each house of 21 retorts, we have the following storage: (a) 6 strong acid receivers, made of 20-lb. lead, 8' 3" in diam. and 2' 10" deep, of capacity about 6 tons each of acid of 1.490 sp. gr. (b) 10 weak pottery receivers, holding about 200 gallons each, or about 1.2 tons of acid of 1.340 gravity.

7. *Niter Cake.* This is handled in two ways, (a) by means of flat pans, (b) by granulators. Up to the present about 80% of the niter cake is tapped into flat cast iron pans; there are 4 of these to each retort, each 12' long, 4' 9" wide and 1' deep. The niter cake can be handled within 5 or 6 hours of the retort being tapped. It is broken up and loaded into trucks which run alongside of the retort houses. To obtain granulated niter cake, the liquid

cake, at a temperature of 180° to 200° C., is run from the retorts into granulators. Two of these accommodate the niter cake from a single retort. The granulator consists of a circular pan 10' in diam. by 2 ft. deep, and granulation is effected by 5 sets of staggered knives fixed to the five arms of the driving shaft, which revolves at a speed of 24 r. p. m., being belt-driven from the main shafting. The machine is set in motion before the cake is run in and after about half an hour's agitation the cake begins to set, finally granulating in $\frac{3}{4}$ hour to an hour. When setting the cake fumes badly, and hooded ventilators should be erected over the machines as the fuming is very destructive to the belt drive, and has given much trouble in consequence. A beveled gear-drive would be preferable on future machines.

At present the granulated material is loaded, by hand into the bogies and is tipped from them by a steam crane into trucks. Eventually it will be discharged from the granulators to a conveyor and taken to a bucket conveyor by means of which it will be lifted to a storage bin. The conveyer and elevator have not yet come into operation. The power required for granulation is at present approximately 15 units per ton of niter cake treated. At present only 7 granulators are in operation. The final layout is 14 granulators for each retort house, i. e., 2 granulators per 3 retorts. To drive these, two 100 h. p. motors are to be installed; one of each is in operation at present.

8. *Firing of Retorts.* The retorts are gas fired, and this method carefully controlled, is perfectly satisfactory. Carelessness in firing, however, easily leads to blows, superheating of the cake, and cracked retorts. Most cases of the cracking of the retort, after only a short life, can be attributed to bad firing. It is difficult to lay down hard and fast rules. Successful firing demands constant coöperation between those firing and those responsible for supervising the distillation. It has been found out that the fire can be lowered safely when the gravity of the distillate reached 1.380 and put out when it reached 1.330. The retort will complete its distillation by means of the heat contained in the brick work, without appreciably lengthening the cycle. This gives a fuel economy and a moderately cool niter cake (180° – 200° C.) and ensures absence of charging blows and less strain on the retort. Over the last six months, fuel composi-

tion per ton HNO_3 has averaged 0.15 tons coal. This figure can be improved upon, it is hoped to reach a figure of 0.12–0.13 tons coal per ton HNO_3 , which calculations show to be attainable.

9. *Capacity of Retort.* A retort working normally on a 14-hour cycle is capable of making 3.0 tons HNO_3 per day. Allowing for retorts off for repairs and rebuilding, it is safe to calculate on a daily output of 2.4 to 2.5 tons HNO_3 per retort installed. Our experience has shown that with the complete installation of 42 retorts, there should be no difficulty in maintaining a weekly output of 660 tons HNO_3 . More than this can only be obtained at the risk of cracking retorts with reduction in capacity later on in consequence. It is only possible to reckon on a $6\frac{1}{2}$ day week for retort working, as the gas flues are burned out once a week.

10. *General Chemical and Physical Data.* Condensing area of Hart condenser (3 banks of tubes, 202 sq. ft.). Cooling capacity per sq. ft., 7–10 CHU's per minute. Average strength of condensed acid, 88% HNO_3 . Average strength of absorbed acid, 55% HNO_3 . Length of cycle, 14 hours. Maximum temp. of retort uptake, 140°C . Acidity of niter cake, 28.5% H_2SO_4 . Overall plant efficiency (not including loss in handling niter), 96.5%.

Niter Bag Washing Plant. 1. *General.* In this plant are washed the empty bags from the niter sheds, the purpose of washing being (a) the recovery of NaNO_3 , (b) the production of clean and salable bags. The general features of the process are as follows. The bags are boiled in one of 3 cylindrical boilers, and are then passed through a series of 4 washing troughs, counter currents to a stream of hot water, the bags being lifted from boilers, and from trough to trough by hand. After leaving the 4th trough the bags are centrifuged in one of two centrifugal machines and finally dried in one of the two Ibis driers. After leaving these the bags are sorted and delivered to the clean bag store. The hot water enters the system at the 4th boiler, and flows forward to the boilers gradually increasing in concentration on its way. From the boilers, when sufficiently concentrated, it is blown by air to an overhead tank, from which it passes through one of the 2 Kestner evaporators and is delivered into mild steel crystallizing pans. The crystals are drained, bagged, and sent to the niter store, the mother liquor being returned to circulation

until it becomes too foul for use, when it is run to waste.

2. *Unwashed Bag Store.* The bags are received in trucks and off-loaded into a store $25' \times 25' \times 10'$, fitted with an off-loading porch. This and all other buildings are constructed of corrugated iron. The bags are brushed and conveyed by trolley to the boilers.

3. *Boilers.* These consist of a perforated steel drum $2' 2''$ diam. and $3' 5''$ deep with $2''$ perforations at $4''$ centers inside a steel boiler, $2' 6''$ diam. and $3' 5''$ deep, with a perforated flat steam coil at the bottom. Here the bags are boiled by means of a pneumatic piston press of the Douglas-Fraser pattern, to free from concentrated liquor as far as possible.

4. *Troughs.* The bags are removed from the boilers by hand into a series of troughs each $12' \times 3\frac{3}{4}' \times 2\frac{3}{4}'$ deep; the last trough is fed from an overhead tank. After passing through the 4 troughs the bags are wrung.

5. *Wringers.* The wringers or hydroextractors, are belt-driven at a speed of 1100 R. P. M., fitted with a basket $36''$ in diam., the drainings being pumped to the 3rd trough by centrifugal pump.

6. *Ibis Driers.* These are $20'$ long by $10'$ wide, the bags at the feed end being clipped to traveling rods, so arranged that when the rod reaches the delivery end, the bags are automatically released. The drying is done by hot air, generated by a $30''$ fan blowing air over a cast iron steam radiator, situated at the delivery end of the machine. Each drier will hold about 200 bags, and will dry approximately 120 bags per hour.

7. *Clean Bag Store.* This is 45 ft. long and 30 ft. wide and 10 ft. high. The bags are delivered here after being dried and sorted:

8. *Feed Tanks and Water Tanks.* The liquor from the boilers is circulated until the gravity is sufficiently high for concentration. When this is reached it is blown by either of 2 blow cases, $15''$ diam. $\times 3\frac{3}{4}'$ long, through either of two filter presses into the main feed tank for the evaporators. Each of these consists of 10 chambers each $20''$ sq., with the necessary inlets and outlets, the chambers being divided by filter cloths. The feed tank to the evaporators is a mild steel tank $4' \times 3\frac{1}{2}' \times 3\frac{1}{2}'$ deep, lagged and fitted with overflow and discharge pipes. The water tank feeding the fourth trough is of the same dimen-

sions, and acts as a receptacle for all the condensed water from the steam traps.

9. *Evaporators.* Two are in operation, of the horizontal Kestner type, consisting of a bank of 4 horizontal tubes $16\frac{1}{2}'$ long, arranged with concentric steam pipes. The concentrated liquor is fed to the bottom of the nest of tubes, and the steam enters at the top, on the countercurrent principle. During its passage through the tubes the liquor is concentrated and is finally discharged into a cast iron separator, the steam escaping to the atmosphere and the liquor running to the launders.

10. *Crystallizing.* The concentrated liquor from the evaporators is distributed into one of the three water-cooled pans to permit of crystallization. These are $15' \times 4\frac{3}{4}'$ being $\frac{3}{4}'$ deep for 10' of their length and grading through the last 5' down to a depth of 1". They are constructed of mild steel plates $\frac{1}{4}"$ thick, and each is set in a cooling pan $15\frac{1}{4}' \times 5\frac{1}{4}' \times 12\frac{1}{4}"$ deep fitted with a water overflow. The nitrate of soda crystallizes out and is removed on to draining boards, the mother liquor being raised back into the circulation tank by means of a steam ejector.

11. *General.* The capacity of the plant for efficient working can be reckoned as 15000 bags per week. The washing yields a bag containing about 7% NaNO_3 and 10% water and about 0.65 tons of nitrate of soda are recovered per day with a water content of $10\frac{1}{2}\%$. The average NaNO_3 content of unwashed bags is about 29%. Bags are charged to each boiler at the rate of 50 bags per hour. Usually two boilers are in operation at once. The completed cycle of operations in the boilers takes about an hour, and the operations in the troughs are phased to this speed. On this load, the evaporators deal with approximately 224 cu. ft. of liquor per day with a 3% NaNO_3 content and deliver 156 cubic feet per day with a 50.5% NaNO_3 content. The NaNO_3 gradient from trough 4 to the boilers averages as follows:

| | % NaNO_3 | Temperature ° C. |
|----------|-------------------|------------------|
| Trough 4 | 15.2 | 36 |
| Trough 3 | 19.6 | 33 |
| Trough 2 | 24.1 | 41 |
| Trough 1 | 30.6 | 75 |
| Boilers | 35.0 | 103 |

The Commercial Utilization of Niter Cake: The fixed residue from the manufacture of nitric acid, formerly called

"Salecnixum," substantially consists of a mixture of neutral and acid sodium sulfate, containing from 29% to 32% free acid and only traces of nitric acid and of nitrate.

Niter cake is, primarily, a mixture of normal sodium sulfate with varying proportions of sulfuric acid, or perhaps more properly, an impure sodium acid sulfate carrying a variable excess of sodium sulfate or, less frequently, of free sulfuric acid. Sodium acid sulfate (sodium bisulfate) contains normally 40.6% sulfuric acid combined with 59.4% sodium sulfate in the double salt of the formula NaHSO_4 . Niter cake may, occasionally, approximate this composition, but its acidity usually ranges between 28% and 34% sulfuric acid, depending on working conditions surrounding its production, and the fluidity of the mass as it emerges from the nitric acid retort.

Niter cake contains small percentages of iron, alumina and silica as usual impurities, or traces of arsenic, sodium nitrate or nitric acid as accidental impurities, if the process of manufacture is improperly carried on. The following analysis, given by E. Corbett, is considered as fairly typical of its average composition:

| | |
|--|--------|
| Silica..... | 0.10% |
| Iron and aluminium oxide..... | 0.45% |
| Free acidity (calculated as H_2SO_4)..... | 34.55% |
| Sodium nitrate..... | 0.05% |
| Sodium sulfate..... | 64.75% |
| Calcium and magnesium sulfates..... | Trace |

Occasionally runs in which impure chamber acid has been used show traces of arsenic, but the occurrence of arsenic in niter cake is usually rare.

Acid salt cake differs from niter cake primarily in the method of its preparation. The former is the corresponding by-product of a hydrochloric acid still and is formed by the treatment of sodium chloride with sulfuric acid, comprizing about 30% free sulfuric acid and 67% 69% sodium sulfate, with traces of hydrochloric acid, chlorine, chlorine oxides, sodium chloride, and those impurities normally present in common rock salt.

Niter cake, therefore, is a chemical compound of indefinite and varying composition which, like sodium bisulfate, or acid sulfate breaks up in solution into sodium sulfate and free sulfuric acid, the latter being entirely available for solvent purposes.

With the outbreak of hostilities in Europe in 1914 an im-

precedented demand was made for nitric and sulfuric acids upon all the civilized countries of the globe and this, in turn, gave rise to a corresponding excess production of niter cake. The number of references to the utilization of niter cake while voluminous, is not nearly as great as the difficulty of disposing of this by-product would suggest. The main reason undoubtedly is found in the lack of time and plant to deal with the huge amount now available without restricting the output of more essential products, or supplying materials in demand for these products. I. Cheeseman¹ describes a process previously proposed by G. Lunge, namely, to neutralize the solution of niter cake by lime (or calcium hydroxide or carbonate), separating the calcium sulfate by filtration or otherwise, running off the solution of sodium sulfate and utilizing these either alone or for the manufacture of "blanc fixe," "lithopone," "ponolith" or "pearl hardening," by precipitation with barium hydrosulfide solution. II. Kirkman² advocates its employment as an absorbent for ammonia in which instance a profitable utilization of the sodium sulfate would be extremely difficult. W. Giles, F. Roberts and A. Boake³ propose to convert ordinary niter cake into "pentasulfate," by the addition of sulfuric acid, claiming this material can be packed in iron drums or ordinary casks and usefully employed for certain commercial purposes. In 1893 M. Prentice was granted patent protection⁴ for the employment of niter cake in the manufacture of superphosphate of lime from the phosphate in the ordinary manner. In the ideas of A. Campbell and A. Walker,⁵ acid sulfates are utilized in the manufacture of nitric and hydrochloric acids, the niter

1. U. S. P. 714145, 1902; abst. J. S. C. I. 1903, **22**, 26, 36; Chem. Zts. 1903, **2**, 375; Mon. Sci. 1903, **59**, 77. According to the process of C. Thorsell and H. Lunden (E. P. 11487, 1915; abst. J. S. C. I. 1916, **35**, 962) in the production of oxalic acid from sodium oxalate containing sodium carbonate and hydroxide, the material is first treated with a solution containing sodium bisulfate and sulfuric acid to obtain acid sodium oxalate and normal sodium sulfate. The acid oxalate is then washed with water and treated with sulfuric acid to produce oxalic acid and a solution containing sodium bisulfate and sulfuric acid, which solution is used for treating a fresh portion of original material after the latter has received a preliminary treatment with either the wash water of the acid sodium oxalate or the mother-liquor from the crystallization of the sodium sulfate produced in the process.

2. E. P. 5703, 1889; abst. J. S. C. I. 1890, **9**, 391.

3. E. P. 11979, 1890; abst. Chem. Centr. 1892, **63**, I, 111. See O. Zahn, F. P. 389898; abst. Mon. Sci. 1909, **71**, 112.

4. E. P. 8902, 1893; Mon. Sci. 1895, **42**, 50.

5. E. P. 9782, 1894; abst. J. S. C. I. 1895, **14**, 482; Chem. Tech. Rep. 1895, **34**, I, 190.

cake being ground with nitrate of soda, potash or common salt and heated to 600°–800° F., whereby nitric or hydrochloric acid is driven off and collected in any suitable manner. W. Garroway¹ takes about 200 parts by weight of niter cake to 100 parts of sodium nitrate, the mixture being heated in a muffle or like furnace, into which steam and air are injected. The nitric acid which passes off may be economically used in the manufacture of ammonium nitrate, white lead or sulfuric acid, according to the claims of the patentee.²

The method of A. Perret³ is to treat vanadium ores with niter cake at the temperature of fusion of the bisulfate, sulfuric anhydride being evolved, which is collected in dry cold air and condensed by the circulation of brine or by other means. The calcined residue is then exhausted with boiling water, the solution after filtering being treated with ammonium chloride. The precipitated ammonium vanadate thus obtained is calcined forming the crude vanadic anhydride. G. Davis⁴ adds clay or bauxite to a hot concentrated solution of niter cake, heating and agitating by means of high pressure steam. On cooling a mass is obtained said to be suitable for sewage precipitation, but is usually worked up by dissolving, crystallizing out the excess of sodium sulfate and then working up for sodium alum. Chem. Fabrik Grünau, Landshoff & Meyer,⁵ incorporates the bisulfate with about 12% of wood shavings and 2% of coke in a retort provided with mechanical agitation, and then heats the mixture until all the sulfur dioxide formed has been driven out, leaving only neutral sodium sulfate.

1. E. P. 6777, 1899; abst. Chem. Ztg. 1901, **25**, 447. In the method of P. Claes (E. P. 318745, 1902; E. P. 1072, 1900; abst. J. S. C. I. 1902, **21**, 1453) for preparing solid, concentrated, portable sulfuric acid, niter cake is melted with sufficient sulfuric acid to give a product solid when cold (containing about three-fourths of its weight of sulfuric acid), in a suitably heated vessel, connected to an exhauster for production of a vacuum. Means are provided for condensing aqueous and nitrous vapors, and the retort has an exit pipe from which the fluid is delivered on to the surface of a slowly revolving drum, cooled internally by water, and from the side of which the solidified material is scraped, to fall between crushing rollers, and thence into suitable receptacles, to be closed air-tight, for storage or for transit.

2. E. P. 2489, 1896; 7066, 1897; abst. Chem. Ztg. 1898, **22**, 695; Mon. Sci. 1898, **52**, 263. E. P. 22395, 1897; abst. Chem. Ztg. 1899, **23**, 127; Mon. Sci. 1899, **54**, 143.

3. E. P. 26881, 1904; abst. J. S. C. I. 1905, **24**, 1175; Chem. Ztg. 1906, **30**, 359; Mon. Sci. 1906, **65**, 178.

4. E. P. 14749, 1903; abst. J. S. C. I. 1904, **23**, 606.

5. E. P. 6898, 1904; abst. J. S. C. I. 1905, **24**, 196; J. Soc. Dyers Col. 1905, **21**, 113.

In the E. Barbier process,¹ niter cake is dissolved to form a solution of 35° to 45° Bé., and when this is cooled about 10° decomposition is said to result with the formation of crystallized sodium sulfate and free sulfuric acid (?). The C. Parker patent² comprehends bringing a solution of niter cake into contact with a large excess of iron, thus forming ferrous sulfate and ammonia, provided there is not nitrate present. The solution is subsequently worked up for ferrous salt, ammonia and sodium sulfate.

In the recovery of sulfuric acid from acid sulfate, F. Benker³ heats the bisulfate mixed with fine sand, powdered silica or other inert material to a dull red heat, neutral sodium sulfate being left. A. Nibelius⁴ dissolves out the acid from niter cake with a volatile liquid which at the same time is not a solvent of the sulfate, removing the latter, and distills the solution under diminished pressure to recover the volatile solvent, sulfuric acid remaining behind. It is obvious that this process must be unduly expensive. The process of J. Mackenzie⁵ consists in first driving off the moisture from niter cake by melting the latter in a salt cake pot after which the charge is placed in a roaster whereby the sulfuric acid is eliminated and condensed by leading into a Glover tower or other suitable apparatus. Klemm⁶ has suggested the employment of sodium bisulfate in sizing paper as a partial substitute for aluminium sulfate in which one part of niter cake has an efficiency equivalent to that of primarily $2\frac{1}{2}$ parts of aluminium sulfate. The required quantity of glue is first added to paper pulp after which 50% to 60% of the formerly employed preparation of sulfate of ammonia, to which is finally added

1. U. S. P. 484546, 1892; abst. J. A. C. S. 1892, **14**, 321. See E. Borias, F. P. 481767, 1916; abst. C. A. 1917, **11**, 3101.

2. E. P. 24639, 1903; abst. J. S. C. I. 1904, **23**, 252.

3. E. P. 1844, 1907; abst. J. S. C. I. 1908, **27**, 225. F. P. 381363, 1907; abst. J. S. C. I. 1908, **27**, 225. D. R. P. 204353, 204703; abst. C. A. 1909, **3**, 825, 1576; Mon. Sci. 1912, **77**, 50, 81; Chem. Zentr. 1908, **79**, II, 1902; 1909, **80**, I, 413; Chem. Ztg. Rep. 1908, **32**, 662, 691; Chem. Zts. 1908, **7**, No. 986; 1909, **8**, No. 1063; Jahr. Chem. 1905-1908, I, 1613; 1909, **62**, 489; Wag. Jahr. 1908, **54**, I, 376; Zts. ang. Chem. 1909, **22**, 169. U. S. P. 899284; abst. C. A. 1909, **3**, 362. F. P. 381863, 1906; abst. J. S. C. I. 1908, **27**, 225; Mon. Sci. 1909, **71**, 101; Chem. Ztg. Rep. 1908, **32**, 276.

4. U. S. P. 873070, 1907; abst. J. S. C. I. 1908, **27**, 23; Chem. Ztg. Rep. 1908, **32**, 41; Mon. Sci. 1908, **69**, 51.

5. E. P. 13907, 1915; abst. J. S. C. I. 1916, **35**, 838; C. A. 1917, **11**, 526. D. R. P. 291775; abst. J. S. C. I. 1916, **35**, 829; Chem. Zentr. 1916, **87**, I, 1048; Chem. Ztg. Rep. 1916, **40**, 217; Zts. ang. Chem. 1916, **29**, 271.

6. Chem. Ind. 1915, **38**, 311.

niter cake to the amount of 20% of the used aluminium sulfate, the niter cake being dissolved in water the concentration of 2% to 2½%. In proceeding by the method devised by H. Howard,¹ an excess of salt and sufficient sulfuric acid is mixed with the acid sodium sulfate to produce normal sodium sulfate, the mixture being then heated in a hydrochloric acid furnace. The Actien-Gesellschaft Dynamit Nobel² have described the preparation of niter cake in a form allowing of immediate calcination for the purpose of manufacturing neutral sulfate and without the necessity of producing HCl. The process of R. Haas³ for the use of niter cake as a partial substitute for aluminium sulfate in the sizing of paper is similar to that of Klemm, previously mentioned.

In attempts to use a preparation of niter cake produced in the textile industries for the extraction of grease from wool, etc. a committee of users of sulfuric acid in the West Riding of Yorkshire⁴ have reported, but the chief difficulty encountered at the present time is the cost of cartage and railway transportation. R. Sindall and W. Bacon suggested niter cake as a substitute for alum to precipitate the rosin as sizing, stating that 100 parts of rosin require 24 parts of acid sodium sulfate for complete precipitation.⁵

Attention is drawn to the observation that niter cake produces a denser precipitate than alum and that the sizing effected

1. U. S. P. 1193552, abst. J. S. C. I. 1916, **35**, 962.

2. D. R. P. 263120; abst. C. A. 1913, **7**, 3823; Chem. Zentr. 1913, **84**, II, 728; Chem. Ztg. Rep. 1913, **37**, 498; Wag. Jahr. 1913, **59**, I, 420; Zts. ang. Chem. 1913, **26**, 519.

3. Chem. Ztg. 1916, **40**, 571; abst. Chem. Zentr. 1916, **87**, II, 529. See also P. Löffler, U. S. P. 1104911. C. Rommenhöller and E. Luhmann, D. R. P. 63189; abst. Ber. 1892, **25**, 817; Jahr. Chem. 1892, **45**, 2701; Wag. Jahr. 1892, **38**, 331; Zts. ang. Chem. 1892, **5**, 498. The A. G. Dynamit Nobel (D. R. P. 263120, 1913; abst. J. S. C. I. 1913, **32**, 909, C. A. 1913, **7**, 3823; Chem. Zentr. 1913, **84**, II, 728; Chem. Ztg. Rep. 1913, **37**, 498; Wag. Jahr. 1913, **59**, I, 420; Zts. ang. Chem. 1913, **26**, 519) have described a process for obtaining sodium bisulfate in a form in which it can be directly calcined, and in which organic substances, preferably cellulosic materials such as sawdust, peat, or the like, are stirred into the fused bisulfate while it is solidifying; vigorous evolution of gas takes place and a loose, spongy, solid product is obtained, containing some carbon, which in the subsequent calcination acts as a reducing agent and is expelled as carbon dioxide.

4. Chem. Trade J. 1916, 28; abst. J. S. C. I. 1916, **35**, 109. See also J. S. C. I. 1915, **34**, 1121.

5. Paper Maker's Monthly J. 1916, **54**, 202; abst. C. A. 1916, **10**, 2799.

is somewhat different. It is necessary, therefore, to know the analysis of the niter cake for best results.¹

According to the Society of Chemical Industry² a committee of the Chemical Society and of that Society has been formed for the purpose of devising ways and means for the better and more complete utilization of niter cake. Some of the methods proposed are heating the cake with common salt thus obtaining hydrochloric acid and salt cake; heating with magnesite in order to produce epsom salts; the replacement of sulfuric acid in the manufacture of superphosphate; roasting with iron scale in order to eliminate the available acid; its complete utilization in the manufacture and glazing of slag bricks; sprinkling on manure heaps in order to conserve and fix the ammonia; heating with mixed sulfide ores to extract zinc; removing the free sulfuric acid by applying superheated steam into the diffused mass; extracting copper from copper pyrites; taking advantage of the free acid to decompose soap suds in the regeneration of the fatty acids contained therein; making blanc fixe and sodium hydrosulfide; conservation of the nitrogen by heating with leather clippings whereby ammonium sulfate results; roasting with feldspar, thus producing potash alum; combining it with salt for the roasting of copper, zinc and nickel ores; converting sodium chromate and other chromates into the corresponding bi-chromates; the treatment of tungsten ores; heating in a salt cake furnace for the recovery of sulfuric acid and sodium sulfate; neutralizing the free acid and reducing the sulfate by means of coal dust to the corresponding sulfide; converting into soda alum and fusing with same, thus producing sulfuric acid and silicate of soda (water glass).

In carrying out the process of I. Llewellyn and P. Spence & Sons³ niter cake is heated with metallic iron or pyrites, sulfur dioxide being evolved and the mixture or sodium sulfate and ferric oxide remaining, from which sodium sulfate may be obtained by crystallization.

According to F. Stanes and G. Rogé,⁴ vitriol may be eco-

1. Paper, 1916, **18**, 2E; abst. C. A. 1917, **11**, 888.

2. J. S. C. I. 1915, **34**, 857, 1121.

3. E. P. 103689, 1916; abst. J. S. C. I. 1917, **36**, 385; C. A. 1917, **11**, 1732.

4. E. P. 29254, 1913; abst. J. S. C. I. 1915, **34**, 227; Ann. Rept. Soc. Chem. Ind. 1916, **1**, 110; Chem. Ztg. Rep. 1915, **39**, 270; Mon. Sci. 1917, **84**, 73.

nominally obtained from sulfur by roasting it with twice its weight of niter cake, or¹ acid sulfate may be heated with sulfur in a muffle, the liberated sulfur dioxide collected while the residual anhydrous sulfite is converted into bisulfite by treatment with sulfuric acid.

C. Budde² has suggested the use of niter cake instead of sulfuric acid in treating paper makers' black liquor for the recovery of carbon dioxide, acetic acid, furfural and ammonia with the eventual reduction of sulfate to sulfite.

J. Fielden uses niter cake to replace sulfuric acid in the souring stages in bleaching textiles or in certain dyeing operations with acid dyes. A solution of 100° Tw. niter cake with 70% vitriol has been recommended for the production of sulfate of ammonia.³ The Sulfate of Ammonia Association⁴ have drawn attention to the fact that the recommendation of using niter cake as a substitute for sulfuric acid in the manufacture of ammonium sulfate has met with somewhat caustic criticisms in as much as this proposal involves the reduction of the amount of ammonia in the sulfate to 74 parts and possibly less. It can therefore be advocated only as a temporary expedient. The presence of free nitric acid in the niter cake causes damage to the leadwork of the saturator by its solvent action and ultimately the destruction of ammonia.

J. Stewart⁵ treats the residues or "foots" obtained in refining oils with alkali, with an acid salt such as sodium bisulfate or a solution of the acid salt, such as niter cake. Not only does the addition promote the saturation of the aqueous layer, but the saturated oil is claimed to be of a lighter color.

In the proposed use of this material as a substitute for sulfuric acid in the pickling of annealed brass, as brought forward by H. Brownsdon,⁶ attention is called to the fact that the quantity of sulfuric acid used for the pickling of annealed brass runs into

1. E. P. 18605, 1914; abst. J. S. C. I. 1915, **34**, 961; Ann. Report Soc. Chem. Ind. 1916, **1**, 113; Mon. Sci. 1917, **84**, 76.

2. J. S. C. I. 1916, **35**, 77.

3. J. S. C. I. 1916, **35**, 109; abst. Ann. Report. Soc. Chem. Ind. 1916, **1**, 114.

4. Chem. News, 1916, **113**, 175; abst. J. Gas Lighting, 1916, 74. See also Chem. Trade J. 1916, **59**, 548.

5. E. P. 101959, 1916; abst. J. S. C. I. 1917, **36**, 557; C. A. 1917, **11**, 545.

6. J. S. C. I. 1917, **36**, 575; abst. C. A. 1917, **11**, 2442.

several hundred tons per day and the present difficulty in obtaining raw material and labor combined with increased demand for sulfuric acid for other purposes has resulted in the constant application of niter cake solution in place of dilute sulfuric acid for the pickling of annealed brass.¹

1. As a pickling agent, niter cake solution is inferior to sulfuric acid and under certain conditions its use leads to very unsatisfactory results. For this reason the subject is of more than passing interest to those who have to deal with the rapid pickling and cleaning of large quantities of annealed brass. The two products controlling the success or otherwise of the process are the niter cake and the annealed brass. Niter cake is essentially crude acid sodium sulfate and while the latter in the pure anhydrous state contains theoretically 40.8% of sulfuric acid, the free acid found in niter cake may vary from 15% to 35%. It is evident that where difficulty may be experienced in obtaining satisfactory results with niter cake poor in free acid, complete satisfaction may be given with better qualities, and in purchasing a by-product of this nature for pickling purposes a minimum content of free acid should be specified. Niter cake invariably contains small quantities of free nitric acid which, however, from a pickling point of view are negligible. For pickling, the niter cake solution should be of such strength as to show 3% to 5% of sulfuric acid on titration and for reasons which may be considered later, there is no advantage to be gained in using solutions of higher acid concentration.

While niter cake is a variable product, annealed brass, from a pickling point of view may be even more so. According to the conditions of annealing, it may be clean, practically free from superficial oxides and of a brassy luster, or it may be dirty, black in color and badly stained through oxidation and contact with injurious furnace gases. Given clean work, niter cake solutions replace dilute sulfuric acid quite efficiently but with dirty work the difference is much more marked and niter cake solution, even under the most favorable conditions may fail to pickle the work satisfactorily. In the latter case the use of niter cake in place of sulfuric acid becomes a serious handicap and deterrent to rapid production, especially when manufacture consists of a sequence of mechanical operations between each of which the product has to be annealed, pickled and cleaned. It is little consolation for the manufacturer to know that his troubles lie in his annealing furnaces, for he cannot equip himself with furnaces of new type in order to overcome difficulties of pickling, and it is for him to see that the niter cake solution is used under the most favorable conditions possible for efficient pickling.

- (a) The niter cake solution should be as hot as possible.
- (b) Its acid content should be tested frequently and maintained at 3% to 5% by the addition of niter cake.
- (c) The hot annealed products may be quenched in water whereby much scale is mechanically loosened and readily recovered prior to pickling.
- (d) The hot annealed work may be placed direct into the niter cake solution. The pickle can thus be maintained at a high temperature without auxiliary steam heating.
- (e) Oxidizing agents such as ferric salts, bichromates, or persulfates may be added in the pickle. Their addition stimulates the solvent action of the niter cake solution, but their action is not constant and in many cases the price is prohibitive.
- (f) Electrochemical aid might be sought by using a low voltage current, making the lead lining of the vat the cathode and the work to be pickled, the anode.
- (g) The movement of the work in the pickle or/and the agitation

J. Hannay¹ calls attention to the fact that whereas niter cake is usually stated to contain 17% to 33% of available sulfuric acid, the samples examined by him contained 35% to 40%, the theoretical value for sodium bisulfate being 40.83%. He draws attention to the fact that difficulty in transporting of this material is considerably enhanced by the marked hygroscopicity of the bisulfate and recommends for the commercial utilization of the niter cake solution that it be dissolved in stone tanks or in wooden tanks lined with lead or asphalt at a concentration of preferably 4 pounds per gallon. If warm water is available, solution is complete in about two hours, but with cold water, the niter cake is required to remain in the water over night. The solution thus obtained contains 10% to 11.5% of available sulfuric acid and there are but few uses to which vitriol is put in calico bleaching and printing where such liquor may not be applied with advantage. He claims that bleachers' goods soured with niter cake are equal in every respect to those soured with of the pickle during pickling.

The difficulties met with in the successful use of niter cake solution can only be overcome in a satisfactory manner by, in the first instance, paying close attention to the conditions governing the annealing so as to obtain the annealed brass as clean as possible, and secondly, by using the niter cake solution under conditions which will most strongly stimulate its pickling activity.

It is quite probable that the action of pickle is not entirely solvent, as between oxide film and acid. In the case of annealed brass being immersed in an acid pickle, all the elements are present for electrochemical action and the difference in potential arising between the metal and the oxides may produce minute local currents which may aid or deter the solvent action of the pickle according to the nature of the free ions present in the pickle, which then becomes the electrolyte.

E. Corbett (Bur. of Mines, 1918, 17 pp.) claims the saving of 10%-20% in expense by the substitution of niter cake for sulfuric acid in the pickling of steel.

H. Le Chatelier and B. Bogitch (Rev. Met. 1915, **12**, 949; abst. J. S. C. I. 1916, **35**, 845) have worked out the following procedure: the first solution is made to contain 25 gm. sodium bisulfate per 100 cc. and is used at 80° until half the sulfuric acid has been consumed. Then 12.5 gm. of bisulfate is added and the bath used a third time. The acid liquid thus charged with ferrous sulfate and on the point of crystallizing is then discarded. Alternately the bath may be cooled to 25°, after adding a third lot of bisulfate, where the double sodium and iron salt which crystallizes is separated, the liquor reheated to 80°, and the volume made up with added water. To ensure that none is wasted, it is better to add the bisulfate dissolved in half its weight of boiling water. It is necessary to control the acidity of the bath by actual tests to avoid loss of bisulfate on the one hand, and undue impoverishment of the bath, on the other.

1. J. Soc. Dyers Col. 1916, **32**, 65; abst. J. S. C. I. 1916, **35**, 418; C. A. 1916, **10**, 2151.

vitriol. According to an order promulgated by the British Ministry of Munitions on and after October 18, 1916, all supplies of sulfuric and hydrochloric acids for bleaching were prohibited and niter cake recommended for use in its place. However, as P. Bean has drawn attention,¹ it is impossible to successfully bleach without using hydrochloric acid, and this applies particularly to goods in which the highest degree of whiteness and purity is demanded. Certain classes of textiles, including those which have to be dyed or printed with alizarin colors, can only be bleached successfully if they are subjected to the lime boil, in which case it is essential to use HCl as sulfuric acid affords insoluble calcium sulfate which is prone to be precipitated in small amounts on the fiber.

In a partial possible substitution of niter cake for sulfuric acid in sulfate of ammonia, P. Parrish² considers that as a purely

1. Chem. Trade J. 1916, **59**, 393; abst. J. S. C. I. 1916, **35**, 1152; C. A. 1917, **11**, 402.

2. Gas J. 1917, **137**, 345; abst. J. S. C. I. 1917, **36**, 336; C. A. 1917, **11**, 2728. More recently (Gas J. 1918, **143**, 395; abst. C. A. 1919, **13**, 69) he has found that, in ammonium sulfate manufacture, by adding ground niter cake to the acid charge pot, a satisfactory mixture of mixed sulfate of NH_4 and Na containing a higher content than 10% of Na_2SO_4 was obtained, as well as economy of working. The H_2SO_4 content of the bath must not fall below 6% or else ferrocyanides may form. The free acid content of the saturator liquor should be determined by titration. The niter cake should be added with regularity and should be of substantially uniform quality. The amount of undecomposed nitrate in the niter cake should also be known, as this is the chief cause of the corrosion of the lead. In one method the niter cake was dissolved in the feed acid in suitable lead-lined tanks placed contiguous to the saturator at such a height that the niter cake acid solution flowed to the saturators by gravity. The lead-work of the dissolving tank corroded so badly that the method was discontinued. This corrosion was due to the use of an inferior quality of niter cake or possibly the use of arsenical acid. A niter cake solution with an approximate content of 6% H_2SO_4 can be fed to the saturator along with the acid in certain fixed proportions. The NH_3 and the steam passing forward from the stills as in ordinary $(\text{NH}_4)_2\text{SO}_4$ plants, or with the coke gas as in direct plants, enters the saturator where absorption occurs and the sp. gr. increases. After time the deposition of $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 occurs. Some of the saturator liquor is ejected into the mother-liquor well and the supply of acid and niter cake solution to the saturator is resumed until the normal level of the bath is restored. On reaching the mother-liquor well the discharged solution cools and on reaching 46° practically all the Na_2SO_4 crystallizes out. The lighter mother-liquor containing NaHSO_4 and $(\text{NH}_4)\text{HSO}_4$ is again pumped to the saturator and a definite series of operations established. A Mond recovery plant at Langworth, Eng., uses the following process: The gases leaving the producer after having been cooled and treated for the extraction of tar, are scrubbed in a tower with a 3%-4% H_2SO_4 solution. On reaching the saturation point, the solution is evaporated and treated to crystallize out the $(\text{NH}_4)_2\text{SO}_4$. The residual mother-liquor is concentrated at

emergency measure, the production of a mixed salt is quite feasible. He thinks damage to the lead work of the saturator need not be feared, for the niter cake does not contain more than 0.5% of undecomposed nitrate. The manurial qualities of the mixed sulfate produced should, according to Rothansted experiments, be satisfactory, due to the decided beneficial action exerted by the sodium sulfate. A mixed salt containing 10% of sodium sulfate is regarded as the limit to substitution in practice. If a quantity of niter cake to attain this is added dissolved in water, the saturator will become too dilute. In the absence of a method of adding the niter cake in the form of a solid, the author recommends introducing it dissolved in a sulfuric acid vat into the bath, the cake being broken up into small pieces, is dissolved in sulfuric acid in a lead-lined tank heated by closed steam coils, and the hot solution then used as saturator feed. By having duplicate tanks, one can be feeding the saturator while a fresh solution is made up in the other. A fairly uniform mixed salt can be made free from undue acidity, it requiring 14.7 tons of niter cake containing 32% sulfuric acid and 87.8 tons of 70% sulfuric acid or 76.8 tons of 80% acid to produce one hundred tons of mixed salt containing 10% of sodium sulfate.

The Metallbank and Metallurgische Ges. and H. Klencke¹ obtain neutral salt cake by heating niter cake in the well known way with concentrated sulfuric acid in a single furnace space, the salt cake formed being in the liquefied state. Their apparatus consists of a trough of highly acid-resisting cast iron resting on a fire clay bed, provided with a cover of fire clay or similar material. The fire gases enter at one end perpendicular to the bath and leave the apparatus at the other end. It is stated for best results that the flame should be clear and not smoky. The niter cake is introduced continuously by mechanical means, the neutral sulfate being removed at the opposite end by several outlets of different about 80° and very little Na_2SO_4 from the niter cake goes into solution. The mother-liquor, containing additional H_2SO_4 , with the niter cake, is used in the tower, and the resulting Na_2SO_4 sludge is washed free of NH_4OH with water, the washings being used to dilute the tower acid. By this process, $(\text{NH}_4)_2\text{SO}_4$ with a content of 24.5% NH_3 and 0.4% H_2SO_4 is being produced, and saleable Glauber's salt can be crystallized out, containing only traces of NH_3 , which appears to be occluded in the crystals of Na_2SO_4 .

1. D. R. P. 274873, 1912; abst. J. S. C. I. 1914, **33**, 788; C. A. 1914, **8**, 2931; Chem. Zentr. 1914, **85**, II, 95; Chem. Ztg. Rep. 1914, **38**, 338; Wag. Jahr. 1914, **60**, I, 340; Zts. ang. Chem. 1914, **27**, 398.

lengths. By this means the maximum yield is obtained.

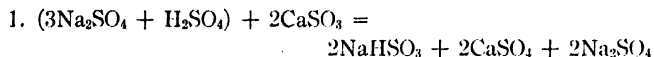
F. Staneş and G. Rogé¹ suggest heating with sulfur in a non-oxidizing atmosphere, collecting the sulfur dioxide and converting the acid sodium sulfate to the normal sulfate by further treatment with sulfur dioxide. J. Grossmann² obtains caustic soda

1. E. P. 18605, 1914; abst. J. S. C. I. 1915, **34**, 961; Ann. Report Soc. Chem. Ind. 1916, **1**, 113; Mon. Sci. 1917, **84**, 76. See also Passmore, E. P. Appl. 6063, 1918; abst. J. S. C. I. 1918, **37**, 227-A. In the recrystallization of niter cake, B. Saxton (J. Ind. Eng. Chem. 1918, **10**, 897; abst. C. A. 1919, **13**, 363) has developed equations for the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 25° by means of which can be calculated (a) how much of any one solid phase will separate from a solution if the composition of the original solute and the acid concentration of the solution after crystallization are known; and (b) the weight of water in the solution after crystallization or the weight of water to be added to the solid niter cake in order to leave a calculated weight of one of the solid phases. Calculations are also made of the maximum amount of each solid phase which can be removed from solution at 25° and 0°. Processes are suggested whereby the H_2SO_4 may be concentrated in the solution and Na_2SO_4 in the solid at the two temperatures mentioned. The separation can be made much more efficiently at the lower temperature.

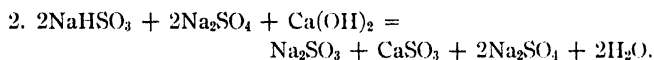
2. E. P. 12832, 1915; abst. J. S. C. I. 1916, **35**, 1059; C. A. 1916, **10**, 1408; 1917, **11**, 878; 1918, **12**, 203, 409, 1501. U. S. P. 1298334, 1919; abst. J. S. C. I. 1919, **38**, 515-A. E. P. 110405, 1916; 114180, 1917; abst. C. A. 1918, **12**, 1501; J. S. C. I. 1917, **36**, 1234; 1918, **37**, 241-A. E. P. 115340, 1917; C. A. 1918, **12**, 1818; J. S. C. I. 1918, **37**, 371-A. E. P. 111875, 1918; abst. J. S. C. I. 1918, **37**, 56-A; C. A. 1918, **12**, 855. E. P. 119290; abst. J. S. C. I. 1918, **37**, 640-A, 733-A; C. A. 1918, **13**, 1686. See also J. S. C. I. 1916, **35**, 155; 1917, **36**, 1035, 1161; 1918, **37**, 103-T, 56-A, 241-A; C. A. 1918, **12**, 1412. C. Goodwin, J. S. C. I. 1917, **36**, 1161. J. Grossmann (E. P. 115340, 1917; abst. J. S. C. I. 1918, **37**, 371-A) obtains niter cake in a disintegrated or ground form by submitting the cake to a certain critical temperature—about 50° for niter cake containing 27% free sulfuric acid, but varying with the content of free acid—the niter cake being disintegrated by crushing or grinding more readily than under ordinary conditions. Accordingly, solidified or hardened niter cake is cooled to the required degree and then disintegrated, the final grinding being completed at or near atmospheric temperature.

In the W. Goulding and J. Osterstetzer process for artificial manure manufacture (E. P. 2335, 1901; abst. J. S. C. I. 1902, **21**, 358; Chem. Ztg. 1902, **26**, 533) a mixture of 10 parts of magnesium carbonate, 20 parts sodium bisulfate, and 70 parts calcium carbonate; or 20 parts sodium bisulfate and 80 parts calcium carbonate, is used to mix with artificial manure containing soluble phosphates with or without potash salts, in the proportion of about 17 parts to 100 parts of the manure. The addition of this "carbonated sodium powder" to an ordinary superphosphate manure is stated to render it fit for use in poor soils deficient in lime. He has found (E. P. 114180, 1917; abst. J. S. C. I. 1918, **37**, 241-A) that when the niter cake, finely ground, is mixed with finely ground sodium nitrate and heated at 150°-250° C., the nitrate is decomposed almost quantitatively with the evolution of nitrous fumes. The proportion in which the substances are mixed will depend on the quantity of free sulfuric acid in the niter cake. The process may be carried on under ordinary, augmented, or diminished pressure, and air may be either excluded from or passed through the apparatus in which the decomposition takes place. If excluded from the decomposing vessel, the air may be mixed with the nitrous fumes subsequently, with formation of nitric and nitrous acids which may be used in the manufacture of sulfuric acid. The

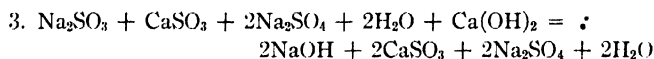
and purified sodium sulfate from niter cake by the following series of reactions:



The calcium sulfate is removed and lime added with agitation.



The calcium sulfite is removed and more lime added.



During reactions 2 and 3 (which may be combined in one operation) heat may be applied and also an augmented pressure. The calcium sulfite is removed, washed, and used over again; the sulfate crystallizes out and after its separation, the liquid is further evaporated, if necessary to dryness. The apparatus for 1 is a leaden tank provided with a cover and stirrer; that for 2 and 3 is similar but means for applying heat is added.

C. Fish¹ has evolved a process of sizing pulp, combining the use of niter cake and aluminium salts, the cake being added after the aluminium salts have been incorporated in the pulp. To the resin size is thoroughly mixed a small quantity of soluble aluminium salts, say one-half to one per cent., calculated on the material in the beater and when these are thoroughly mixed the niter cake is then added.

D. Morgan² has suggested a method for the utilization of mixture may be placed on trays carried by trolleys which are introduced into the decomposing chamber at one end where the temperature is below 150° and discharged at the other end, the temperature of which is about 250°. Also (E. P. 111875, 1916; abst. J. S. C. I. 1918 **37**, 56-A) that by heating a mixture of sodium nitrate, niter cake, and carbonaceous material in suitable proportions to about 250°, the nitrogen is evolved almost entirely as nitric acid or oxides easily oxidized to nitric acid, there being no nitrogen nor nitrous oxide formed; the residue is an easily friable form of slightly acid sodium sulfate with carbonaceous material. The process may be conducted at ordinary, increased, or reduced pressure, and air may be blown or drawn through part or all of the system. The evolved nitrous gases may be treated with air and steam for the production of nitric acid or passed to a sulfuric acid plant.

1. E. P. 16742, 1915; abst. C. A. 1917, **11**, 1547; J. S. C. I. 1917, **36**, 132. Cf. E. Hart, J. I. Eng. Chem. 1918, **10**, 238; abst. C. A. 1918, **12**, 980.

2. Econ. Proc. Roy. Dublin Soc. 1917, **2**, 238; abst. J. S. C. I. 1917, **36**, 504. See also A. Campbell and A. Walker, E. P. 9782, 1894. In the process of J. Morgan (E. P. 128302, 1917; abst. C. A. 1919, **13**, 2981; J. S.

niter cake which avoids serious loss of either sulfur or alkali and also eliminates in a large measure the difficulties of transit and storage of the salt. He found that when niter cake is heated with sand, sulfuric acid is evolved and a soda frit obtained which, however, still contains notable amounts of sulfate. Increase of the proportion of sand reduces the amount of residual sulfate, and this is still further minimized by the use of charcoal, sulfur and sulfur dioxide being then formed along with the sulfuric acid. It is claimed that the soda frit may be advantageously converted into a glass by melting with suitable oxides. If the use of fluorides is avoided the recovery of the sulfur and the formation of a glass may be carried out at one operation, the retort being connected with the sulfuric acid plant.

L. Sherwood¹ utilizes the heat from the combustion of sulfur to heat niter cake and to effect decomposition of the latter into sulfur dioxide and sodium sulfate. The latter is recovered as such and the sulfur dioxide produced by the decomposition and by the combustion is converted into sulfuric acid.

E. Hart² dissolves the niter cake in water to form a solution of about 1.30 sp. gr., and this solution is cooled to about -40° whereby the sodium sulfate crystallizes out in a granular mass. R. Lamb³ prefers to wash with sodium chloride and to recover the niter by means of the difference in solubility. In the process of the Societe Industrielle le Produits Chimiques⁴ the niter cake is dissolved in water and treated with an excess of gaseous ammonia, after which the solution is saturated with carbon dioxide.

C. I. 1919, **38**, 484-A) niter cake is heated in a closed chamber to produce neutral sulfate, and this, while still hot, is further heated in the closed chamber with a material, such as slag, which will drive out the combined acid. The opening statement refers to the decomposition of Na_2SO_4 by SiO_2 or Al_2O_3 . The particular process described consists in placing the niter cake on the surface of molten basic slag which drives off the free acid, and then breaking the crust and stirring the residue into the body of the molten slag. This removes the combined acid and leaves the slag in a form more suitable for setts and for fertilizer. Cf. E. P. 14780, 1885; 1844, 1907; 273, 1908; abst. J. S. C. I. 1908, **27**, 225, 898.

1. U. S. P. 1255474, 1918; abst. C. A. 1918, **12**, 982; J. S. C. I. 1918p **37**, 206-A. In this connection see J. Johnston, J. I. Eng. Chem. 1918, **10**, 468; abst. C. A. 1918, **12**, 1490.

2. U. S. P. 1258895, 1918; abst. C. A. 1918, **12**, 1413; J. S. C. I. 1918, **37**, 302-A.

3. U. S. P. 1242355, 1918; abst. C. A. 1918, **12**, 207; J. S. C. I. 1917, **36**, 1227.

4. E. P. 109814, 1917; abst. C. A. 1918, **12**, 207; J. S. C. I. 1918, **37**, 345-A.

The precipitated sodium bicarbonate is washed and dried, and the mother-liquor, after neutralization with niter cake solution, is diluted and cooled to or below zero to separate the sodium sulfate. The solution is then concentrated in vacuo to recover the ammonium sulfate. C. Godber¹ uses niter cake with salt in the manufacture of HCl and salt cake in a mechanical furnace at about 600° where the sources of supply contain from 29.5%-32% sulfuric acid.

The Gewerkschaft Amelie² first roast the sodium acid sulfate with an excess of KCl to produce acid potassium sulfate. According to C. Goodwin³ the rational utilization of niter cake lies in the manufacture of HCl of high strength which would displace both niter cake and sulfuric acid in many non-essential industries.

In the industrial utilization of fertilizers, according to the method of L. Angibaud,⁴ in addition to the substance named in the chief patent,⁵ sodium bisulfate has been found also to dissolve horn, leather, furs, wool, skins, bones and glue residues.

In a process for producing soluble potassium compounds, as evolved by H. Bassett,⁶ a mixture of the insoluble silicate containing potassium with an alkali acid sulfate, and another salt capable of absorbing sulfur trioxide, is heated progressively to the decomposition temperature of the acid sulfate. The sulfur trioxide gas liberated by the reaction is led back and brought into contact with the mass at the commencement of the heating, when it is again absorbed and brought into action.

In the production of hydrogen, pure Glauber salts, and a gas purifying mass from iron scrap and sodium bisulfate,⁷ a solution of the bisulfate of sp. gr. 1.16 is added to scrap iron in a suitable tank and is heated by steam to 90°, the liberated hydrogen being washed and collected in a holder. The resulting solution of ferrous and sodium sulfates is then treated with an excess of pow-

1. J. S. C. I. 1918, **37**, 48-T. See also 1917, **36**, 1216-A. C. A. 1918, **12**, 743, 1109. Anon., J. S. C. I. 1917, **36**, 1216-A; abst. C. A. 1918, **12**, 743.

2. D. R. P. 282253, 1913; abst. C. A. 1915, **9**, 2435; Chem. Zentr. 1915, **86**, I, 515; Chem. Ztg. Rep. 1915, **39**, 73; Zts. ang. Chem. 1915, **28**, 145.

3. J. S. C. I. 1917, **36**, 1161; abst. C. A. 1918, **12**, 517.

4. First addn. to F. P. 339820, 1912; abst. J. S. C. I. 1913, **32**, 619.

5. F. P. 339820, 1904; abst. J. S. C. I. 1904, **23**, 720; Mon. Sci. 1906, **65**, 43.

6. U. S. P. 1217388, 1917; abst. J. S. C. I. 1917, **36**, 455.

7. P. Becquevort and C. Deguide, R. P. 107807, 1916; abst. J. S. C. I. 1917, **36**, 962.

dered lime, producing a mixture of calcium and ferrous hydroxide, which is aerated to convert the latter into ferric hydroxide. The mass is filter-pressed and the solution flowing away is concentrated to a sp. gr. of 1.26, Glauber salt being separated by crystallization. The material left in the filter press is used as a gas purifying agent.

In the H. Brandenburg and A. Weyland¹ process for the extraction of tin from dross, slag, and waste, the powdered material is mixed with water and heat treated with a mixture of one part of hydrochloric acid with two parts by volume of sulfuric acid, no extraneous heating being needed; and the tin dissolved is separated from the filtered solution by known means. It is claimed that sodium chloride may with advantage replace hydrochloric acid in the process, or the sulfuric acid may be replaced by sodium bisulfate, in which case it is necessary to heat the mixture.²

E. Bromme and R. Steinau,³ recover zinc and galvanized iron articles by treating the articles in the presence of an excess of water with a mixture of alkali bisulfate and alkali or alkaline earth chloride.⁴

The concrete waterproofing composition of C. Ellis⁵ consists of an acid sludge, such as is produced by dissolving acid sodium sulfate in water, which is treated with an equivalent quantity, or with an excess of lime and admixed with pulverulent material.

In the production of formic esters from sodium formate, according to the patent of P. Engelskirschen,⁶ a mixture of alcohol, sodium formate and sodium bisulfate is heated, and the formic ester is distilled off under ordinary pressure if its boiling point is below 100°, or under reduced pressure if the boiling point of

1. E. P. 16377, 1903; abst. J. S. C. I. 1903, **22**, 1090.

2. E. P. 21424, 1901; abst. J. S. C. I. 1902, **21**, 976.

3. U. S. P. 1042315, 1912; abst. J. S. C. I. 1912, **31**, 1082; C. A. 1912, **6**, 3400; Mon. Sci. 1913, **79**, 103. D. R. P. 285923, 1913; abst. J. S. C. I. 1915, **34**, 1151; Chem. Zentr. 1915, **86**, II, 451; Chem. Ztg. Rep. 1915, **39**, 304; Zts. ang. Chem. 1915, **28**, 438.

4. Cumming, Romanes and Walker, E. P. Appl. 2728, 1917; abst. J. S. C. I. 1917, **36**, 23.

5. U. S. P. 1077689, 1913; abst. J. S. C. I. 1913, **32**, 1157; C. A. 1914, **8**, 231.

6. D. R. P. 255441, 1911; abst. J. S. C. I. 1913, **32**, 380; C. A. 1913, **7**, 1587; Mon. Sci. 1916, **83**, 59; Chem. Zentr. 1913, **84**, I, 349; Chem. Ztg. Rep. 1912, **36**, 49; Wag. Jahr. 1912, **58**, II, 31; Zts. ang. Chem. 1913, **26**, 114.

the ester is above 100°. The esters are stated to be obtained in very good yields and of substantially neutral reaction.

In the manufacture of sulfuric acid from niter cake, as perfected by F. Freeth,¹ niter cake, calcium sulfate and water are mixed in the proportion of 689:180:313, and heated to 50° with constant stirring until a solution saturated with sodium bisulfate is formed. The double salt $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$ and calcium sulfate are produced. The precipitated double salt containing some calcium sulfate is separated and the solution cooled to 25° until sodium bisulfate separates out. This is removed and the solution concentrated until it contains 70%-75% of sulfuric acid, and is then cooled to 25°, the remaining sodium sulfate being deposited as an acid salt. After separation of this substance the solution contains 75%-80% of sulfuric acid with less than 1% of sodium sulfate. The sodium bisulfate and the sodium acid sulfate obtained as above are then treated with more calcium sulfate, and this cycle of operations repeated. The double salt $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$ is decomposed by extracting it with hot water, the sodium sulfate passing into solution while the greater portion of the calcium sulfate remains insoluble. Temperatures much higher or lower than 50° are said to be unfavorable to the main reaction.

The A. French process for the treatment of refractory zinc-lead ores,² comprises first roasting the ore and then mixing with from 5%-15% (calculated on the original ore) of pulverized sodium bisulfate. The mixture is heated to dull redness in a reverberatory furnace, the temperature being kept below the sintering point in order to retain the mass in a loose powdery form, and then, after cooling, the soluble sulfates are recovered by lixiviation with water containing a small proportion of sodium bisulfate. The above process is intended especially for the commercial separation of zinc and manganese from complex ores.

In the manufacture of concentrated colorless acetic acid from crude pyroligneous acid, G. Glock,³ adds sodium bisulfate

1. E. P. 117649, 1917; abst. J. S. C. I. 1918, **37**, 579-A; C. A. 1918, **12**, 2067; Chem. Trade J. 1918, **63**, 170; Chem. Zentr. 1919, **90**, II, 243.

2. U. S. P. 1041060, 1912; abst. J. S. C. I. 1912, **31**, 1082; C. A. 1912, **6**, 3400; Mon. Sci. 1913, **79**, 103; Chem. Ztg. Rep. 1913, **37**, 24.

3. D. R. P. 130439, 1901; abst. J. S. C. I. 1902, **21**, 721; Mon. Sci. 1902, **58**, 183; 1903, **59**, 706; Chem. Centr. 1902, **73**, I, 1138; Chem. Ztg. 1902, **26**, 389; Chem. Zts. 1903, **2**, 91; Jahr. Chem. 1902, **55**, 815; Wag. Jahr. 1902, **48**, II, 7.

to crude pyroligneous acid, the major portion of the tarry matter present being separated, which collects as an oily layer on the surface. After removal of this layer, distillation of the aqueous portion is said to yield a nearly pure acid, the first fraction being the most concentrated.

C. Hansen¹ obtains free sulfur and sodium sulfate by heating together a mixed solution of bisulfate and sulfite, in the molecular proportion 2:1, under pressure for four or five hours, at a temperature of 160°–170°.

In a pickling process for copper, assigned to the Western Cartridge Company by E. Hitch,² copper and metals containing copper are cleansed by pickling in a bath containing sodium bisulfate and an oxidizing agent, such as sodium or potassium bichromate. In the general pickling of metal goods,³ the articles may be immersed in an acid bath to which is added a small quantity of waste sulfite liquor which has been freed from sulfites by precipitating with a basic calcium compound and filtering off the precipitate.

E. Kendall⁴ proposes to sulfonate coal-tar dyes by first converting sodium acid sulfate into disulfate, which is "persulfated with one chemical equivalent of monohydrated sulfuric acid and the pulverized dehydrated coal-tar dye to be sulfonated being then added to the fused mass; after thorough admixture until sulfonation of the dye is effected, the mass is dissolved in water, the excess of sulfuric acid removed with an equivalent amount of calcium hydroxide, and the filtrate evaporated to dryness."

In obtaining hydrochloric acid, sodium sulfate, and magnesium sulfate, according to the patent of W. Kerr,⁵ a mixture of niter cake and magnesium chloride in the proportion of 2 molecules of the former to one of the latter, is heated with a little water to about 200°, whereby hydrochloric acid is evolved and a

1. U. S. P. 1101740, 1102911, 1913; abst. C. A. 1914, **8**, 2926, 3101; Mon. Sci. 1914, **81**, 177.

2. U. S. P. 1206220, 1916; abst. J. S. C. I. 1917, **36**, 89. The process of W. Hyatt and E. Fellowes (E. P. 116181, 1917; abst. J. S. C. I. 1918, **37**, 426-A; Mon. Sci. 1919, **86**, 23) is similar.

3. A. Hoffman and W. Parkin, U. S. P. 1221735, 1917; abst. J. S. C. I. 1917, **36**, 556.

4. U. S. P. 1217462, 1917; abst. J. S. C. I. 1917, **36**, 500; Mon. Sci. 1917, **84**, 71.

5. U. S. P. 1203357, 1916; abst. J. S. C. I. 1916, **35**, 1260; Mon. Sci. 1917, **84**, 50.

mixture of sodium and magnesium sulfates remain.

R. Kruegener¹ prepares oxidizing baths for photographic purposes by means of a solution containing potassium permanganate and sodium bisulfate, which are especially applicable for the reversal of images.

In the manufacture of hydrochloric acid and sodium sulfate, according to T. Meyer's process² a mixture of sodium chloride and bisulfate is heated to about 400°, the HCl evolved being absorbed by water, and sodium sulfate remaining as a residue.³

M. Muller⁴ has obtained patent protection for a method of precipitating and coagulating viscose by the use of acid sodium sulfate. His process for utilizing sulfate-cellulose waste liquor⁵ comprizes roasting sodium bisulfate in a furnace under reducing conditions with waste liquor from the digestion of sulfite pulp. The free sulfuric acid of the bisulfate is reduced to sulfurous acid, which may be employed for the preparation of fresh sulfite liquor.

In the preparation of sodium sulfate and concentrated hydrochloric acid gas, the Societe K. Oehler,⁶ employ finely powdered sodium bisulfate and a suitable proportion of sodium chloride are intimately mixed, and the mixture heated below redness in a closed vessel provided only with an exit tube or tubes for the gas. Triable sodium sulfate is said to remain in the retort.⁷

In the production of sulfuric acid from sulfates or bisulfates of industrial origin, or from minerals of complex constitution (glauberite or alunite) with the production of caustic alkalis or alkali salts, aluminium sulfate, or purified aluminium oxide, the Societe Diro Fils⁸ have found that the process is dependent upon the affinity of aluminium for alkalis, so that when employed in

1. D. R. P. 198061, 1907; abst. J. S. C. I. 1908, **27**, 834; Chem. Ztg. Rep. 1908, **32**, 356; Wag. Jahr. 1908, **54**, 11, 497.

2. T. Meyer, U. S. P. 702877, 1902; abst. J. S. C. I. 1902, **21**, 971; Chem. Ztg. 1902, **26**, 635; Mon. Sci. 1902, **58**, 184; Chem. Zts. 1903, **2**, 275.

3. Morris, E. P. Appl. 10874, 1917; abst. J. S. C. I. 1917, **36**, 73.

4. U. S. P. 836452; abst. Mon. Sci. 1907, **67**, 115.

5. D. R. P. 297374, 1916; abst. J. S. C. I. 1917, **36**, 870; Chem. Ztg. Rep. 1917, **41**, 148.

6. F. P. 318386, 1902; abst. J. S. C. I. 1902, **21**, 1454; Mon. Sci. 1903, **59**, 121.

7. U. S. P. 698704, 702877, 1902; abst. J. S. C. I. 1902, **21**, 772, 971; Chem. Ztg. 1902, **26**, 461, 635; Chem. Zts. 1903, **2**, 9, 275; Mon. Sci. 1902, **58**, 183, 184.

8. F. P. 417816, 1909; abst. C. A. 1912, **6**, 1966; Mon. Sci. 1913, **79**, 85; Chem. Ztg. Rep. 1910, **34**, 622; 1911, **35**, 321.

a material which does not contain aluminium, this must be added in the form of beauxite or aluminium sulfate. The process is favorably carried out in a muffled furnace in order to obtain the sulfur dioxide and sulfur trioxide free from combustion gases.

M. Sohoni¹ has described an effervescing mixture containing sodium acid sulfate or sodium pyrosulfate in combination with carbonates.

In the manufacture of neutral calcined sulfate and sulfuric acid from bisulfate,² the latter is subjected in a state of fine subdivision to the action of highly heated gases such as air, steam, or a mixture of these, or fire gases, whereupon the bisulfate is split into neutral sulfate and hydrated sulfuric acid.

The process of C. Wuerster³ for the sizing of paper embraces the use of sodium bisulfate, either alone or in conjunction with an aluminium salt for decomposing the rosin soap in the sizing of paper. The object is to obtain the sizing substance in the form of free rosin and to decompose any aluminium resinate which may be produced.

J. Beveridge⁴ heats niter cake with carbonaceous material in a non-oxidizing atmosphere at a temperature which converts the acid sulfate into a normal salt, the sulfur dioxide and trioxide evolved being recovered as sulfite and sulfuric acid respectively. H. Foote⁵ has summarized the literature concerning the solu-

1. U. S. P. 1228252, 1917; abst. J. S. C. I. 1917, **36**, 872. See also S. Trivick, U. S. P. 728335, 1903; abst. J. S. C. I. 1903, **22**, 742, 1130; Chem. Zts. 1903, **2**, 650.

2. D. R. P. 226110, 1909; abst. C. A. 1911, **5**, 1175; Mon. Sci. 1914, **81**, 87; Chem. Zentr. 1910, **81**, II, 1173; Chem. Ztg. Rep. 1910, **34**, 498; Chem. Zts. 1911, **10**, No. 2387; Jahr. Chem. 1910, **63**, I, 527; Wag. Jahr. 1910, **56**, I, 445; Zts. ang. Chem. 1910, **23**, 2294.

3. U. S. P. 695778, 1902; abst. J. S. C. I. 1902, **21**, 636.

4. U. S. P. 1315811, 1919; abst. J. S. C. I. 1919, **38**, 819-A; C. A. 1919, **13**, 2981. Can. P. 192815, 1919; abst. C. A. 1919, **13**, 2746.

5. J. Ind. Eng. Chem. 1918, **10**, 896; abst. J. S. C. I. 1918, **37**, 765; C. A. 1918, **12**, 2477. In this connection see B. Johnston, J. Ind. Eng. Chem. 1918, **10**, 468. W. Herz, Zts. anorg. Chem. 1912, **73**, 274. J. Van't Hoff and C. Van Deventer, Zts. physik. Chem. 1887, **1**, 170. H. Roozeboom, Zts. physik. Chem. 1888, **2**, 513. J. Koppel, Zts. physik. Chem. 1902, **42**, 1; 1905, **52**, 385. F. Schreinemakers and D. van Prooije, Proc. Akad. Wetenschappen **15**, 1326; abst. C. A. 1914, **8**, 1068. A. Massink, Zts. physik. Chem. 1917, **92**, 351; abst. C. A. 1917, **11**, 3184. H. Le Chatelier and B. Bogitch, Rev. Metall. 1915, **12**, 949; abst. C. A. 1916, **10**, 2460. F. Cameron and A. Seidell, J. physik. Chem. 1901, **5**, 649. J. van't Hoff, Zts. anorg. Chem. 1905, **47**, 244. F. Kenrick, J. physik. Chem. 1908, **12**, 693. F. Wirth, Zts. anorg. Chem. 1913, **79**, 360. D. Florentin, Bull. Soc. Chim. 1913, **13**, 362. J. Bell and W. Taber, J. physik. Chem. 1908, **12**, 171. H. Fpote, J. A. C. S. 1915, **37**, 288. E. Volkhonskii, J. Russ. Phys. Chem.

bility of systems relating to niter cake and sodium sulfate.

The fertilizer of P. Carter¹ comprizes cyanamide, niter cake and "fertilizer stick."² One bath chrome liquors,³ and in lieu of sulfuric acid for the solution of zinc slimes⁴ have also been put forward as desirable outlets for this product, as are the patented processes for the manufacture of ammonium sulfate,⁵ and for glass production.⁶ The P. Shuey fertilizer consists of ground phosphate rock and molten niter cake.⁷ The solubility and recrystallization of sodium sulfate acid has been determined by J. D'Ans,⁸ P. Pascal⁹ and B. Saxton.¹⁰

In the cleansing of diamonds, M. Schuyten recommends¹¹ in order to avoid injuring the health of the workmen, that after being ground, the diamonds be cleaned by treatment with fused potassium or sodium bisulfate instead of, as usual, by boiling with sulfuric and nitric acids. Good results have been obtained with

Soc. **41**, 1763; abst. C. A. 1911, **5**, 617. F. Cameron and J. Breazeale, J. physik. Chem. 1903, **7**, 571. A. Hoffman, Zts. ang. Chem. 1910, **23**, 1672.

1. U. S. P. 1293029, 1919; abst. J. S. C. I. 1919, **38**, 333-A.

2. P. Carter, U. S. P. 1279838, 1918; abst. J. S. C. I. 1919, **38**, 24.

3. J. Churchill, Shoe and Leather Rep. Oct. 24, 1918; J. Amer. Leather Chem. Assoc. **13**, 607.

4. W. Cullen, J. Chem. and Metall. Soc. of S. Africa, 1902, (4), **3**, 37; abst. J. S. C. I. 1902, **21**, 1296.

5. H. Dawson, E. P. 125311, 127677, 1918; abst. J. S. C. I. 1918, **38**, 446-A, 361-A, 535-A. J. S. C. I. 1919, **38**, 98; abst. C. A. 1919, **13**, 1613. J. C. S. 1918, **113**, 675; abst. J. S. C. I. 1918, **37**, 577-A; C. A. 1918, **12**, 2290; Mon. Sci. 1919, **36**, 46.

6. According to H. Galt (U. S. P. 1312782, 1312783, 1312784, 1919; abst. J. S. C. I. 1919, **38**, 723-A; C. A. 1919, **13**, 2577, 2584) niter cake is used as a substitute for salt cake in glass manufacture, after neutralizing the free acid of the niter cake by the addition of an alkali such as sodium carbonate, lime or limestone. Neutralization of the niter cake in this manner prevents corrosion of the glass pots or surrounding metal objects and avoids any possibility of harmful effects of "salt water" in the molten batch. "A glass bath may, e. g., be formed of sand 1000, sodium carbonate 298, a preformed mixture of niter cake 50 and sodium carbonate 16 parts, sodium chloride 25, limestone 309, coal 3 and arsenious oxide 5 parts, or sand 1000 mixture of niter cake 607.5 and limestone 179 parts (calcined), limestone 181 and coal 45 parts; or sand 1000, mixture of calcium hydroxide 138 and niter cake 600 parts (calcined), limestone 330 and coal 45 parts.

7. P. McG. Shuey, U. S. P. 1293220, 1919; abst. J. S. C. I. 1919, **38**, 333-A; Mon. Sci. 1919, **36**, 48.

8. Ber. 1906, **39**, 1534; abst. Zts. anorg. Chem. 1906, **49**, 356; 1909, **61**, 91; J. S. C. I. 1906, **25**, 534.

9. Compt. rend. 1917, **164**, 628; abst. J. S. C. I. 1917, **36**, 594.

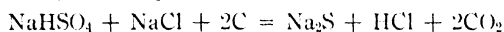
10. J. Ind. Eng. Chem. 1918, **10**, 897; abst. J. S. C. I. 1918, **37**, 765.

11. Handelingen van het achtste Vlaamsch Natuur-en Geneeskundig Congress, gehouden te Antwerpen on Sept. 25, 1904; abst. Chem. Centr. 1905, **76**, I, 411; J. S. C. I. 1905, **24**, 196.

niter cake in paper sizing in the hands of J. Stephenson,¹ while Steinhart and Vogel² produce neutral sodium sulfate and acetic acid from niter cake and an alkaline or alkaline earth acetate.

In the preparation of superphosphate, it is recommended to mix finely ground Florida pebble phosphate, Canadian apatite and powdered niter cake, the only apparatus required being grinding and mixing machines.³ In the W. Kee patent,⁴ niter cake is so heated that it evolves sulfur trioxide and forms salt cake. Solid sodium sulfate is then added to cause solidification of the mass. The process of L. Springer⁵ is similar.

R. Haack⁶ prepares hydrochloric acid from niter cake and salt according to the equation:



For the production of ammonium sulfate,⁷ niter cake ammonium sulfate and sodium sulfate are mixed in the presence of water; a portion of the sodium sulfate is separated, and the solution used without addition of ammonia for the absorbing ammonia from gases containing the same.

Hough Niter Cake Flaking Machine, for handling niter cake (Fig. 52), consists of a single drum mounted on a hollow shaft, attachments being made at one end of the shaft by means of which water of the desired temperature is introduced to the drum. This water leaves the drum from the other end of the shaft.

The niter cake in a molten condition laps against the cool drum, the latter revolving at a speed of approximately 10 r. p. m. About two-thirds of the way around the drum, a doctor or knife is affixed, being supported on a carriage having an adjustment which enables the operator to advance or recede the knife as

1. J. S. C. I. 1918, **38**, 128-T; abst. C. A. 1918, **12**, 1598. See also Sindall and Bacon, Paper, 1916, **18**, No. 24, 22; Paper Makers Monthly J. 1918, **56**, 229. Paper Making, **37**, 378.

2. E. P. Appl. 28799, 1902; abst. J. S. C. I. 1903, **22**, 56.

3. F. Shutt and L. Wright, Royal Soc. Canada, 1918; abst. Can. Chem. J. 1918, **2**, 314; abst. J. S. C. I. 1919, **38**, 83-A.

4. U. S. P. 1313192, 1919; abst. J. S. C. I. 1919, **38**, 718-A; C. A. 1919, **13**, 2576.

5. Keram. Rundschau, 1916, **24**, 3, 115; 1917, **25**, 63; abst. J. Soc. Glass Tech. **1**, II, 4; 1918, **2**, 2672; C. A. 1917, **11**, 3105; 1918, **12**, 2672.

6. D. R. P. 126601; abst. Wag. Jahr. 1901, **47**, 1, 480; Chem. Ztg. 1901, **25**, 1117; Zts. ang. Chem. 1901, **14**, 1284; Chem. Centr. 1901, **72**, II, 1372; Jahr. Chem. 1902, **55**, 537; Chem. Zts. 1902, **1**, 280, 384; Mon. Sci. 1902, **58**, 71.

7. C. Bailey, H. Denny and W. Norris, U. S. P. 1325605, 1919; abst. J. S. C. I. 1920, **39**, 156-A.

desired. The niter cake then falls from the drum in the form of flakes.

A recent improvement has been made in the nature of a micrometer adjustment, which enables the operator at will to change the angle of the knife edge to compensate for the slight wear

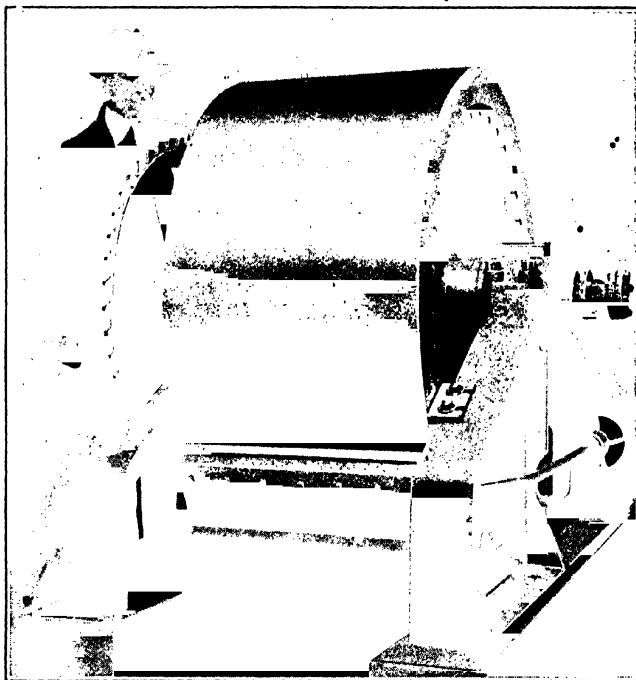


FIG. 52.—HOUGH NITER CAKE FLAKER

that is bound to develop after the machine has been in operation for a few hours. To this end a knife is firmly secured to a substantial carriage having a forward adjustment. The carriage itself is supported on a heavy shaft which is attached to a gear or worm, the worm shaft terminating in a wheel. The operator, by giving the wheel a half turn, can change the angle of the cutting edge. By this means, in the event of the knife riding on

the drum, it can instantly be brought into a cutting position by the means described.

Those with experience, appreciate that the main trouble with flaking machines exists in the riding of the knife over the substance to be removed from the drum. The improvements of Hough as above outlined, are claimed to completely remove this difficulty.

Analysis of Niter Cake. The sample as received is roughly broken up and quartered until about one pound remains. This is then ground in a mortar rapidly and again quartered, leaving a sample of about 100 gm. for analysis.

Total Acidity. 5 gm. are dissolved in water and the solution titrated with $N/1$ NaOH solution, using methyl orange as indicator. The result obtained is expressed as % H_2SO_4 .

Insoluble. 20 gm. are dissolved in water and the solution clarified by paper filtration, the filter having been previously tared by drying for 2 hours at 100° and weighed. The filter paper and residue are then washed several times with hot distilled water and finally dried for 2 hours in a steam oven. From the gain in weight of the filter paper the per cent. of insoluble in the niter cake is calculated.

Iron. 20 gm. are dissolved in water and the solution neutralized with $N/NaOH$ and a few drops of ammonia added to the neutralized solution which is then filtered. The precipitate is washed, then taken up in a few cc. dilute sulfuric acid, the solution being collected in a 100 cc. measuring flask. Any iron present is reduced to the ferrous state by adding a small piece of zinc, and after the reaction is complete the solution is diluted to exactly 100 cc. An aliquot portion of the solution is then withdrawn and titrated with $N/100$ $KMnO_4$.

Nitric Acid. 5 gm. are weighed out and dissolved in 20 cc. water and 100 cc. conc. H_2SO_4 added to the solution. The liquid is then titrated against standard ferrous ammonium sulfate solution as described elsewhere in this volume, and the result found calculated as percentage of HNO_3 .

Nitrous Acid. 5 gm. are weighed out into an Erlenmeyer flask and dissolved in water. 20 cc. $N/100$ $KMnO_4$ is then added and the excess of the latter titrated back with $N/100$ ferrous ammonium sulfate. The result is calculated as percentage

of HNO_2 . The amount of nitrites* is usually small.

Arsenic. 10 gm. are dissolved in 50 cc. water in a 50 cc. flask which has the calibration mark at the base of the neck. A little zinc is added and the Gutzeit test carried out.

Tar and Other Impurities. When carrying out all of the above tests a close examination of the solutions is made for any indications of the presence of tarry matter or other impurities in the sample.

The Manufacture of Nitric Acid and Caustic Soda Simultaneously. Of the many processes that have been brought forth for the decomposition of sodium nitrate so that caustic soda is formed in addition to nitric acid, but although theoretically these processes offer enormous possibilities, none are in large production up to the present time. Their points of superiority are no waste of sulfuric acid and no production of niter cake which is practically valueless, the soda being transformed into caustic soda or the carbonate—its most valuable forms. The difficulties heretofore encountered have been that the temperature of decomposition has been so high, with a correspondingly greater wear and tear on the retorts, while often a considerable portion of the nitric acid is reduced to the lower oxides, recoverable only with difficulty and with considerable loss. Furthermore, the production of nitric acid is not sufficiently great to meet the demands of explosives manufacturers.

In 1861¹ J. Malcolm proposed to mix sodium nitrate with sea sand or other inert material in a retort, nitrous fumes passing over and collected in water while the caustic soda remaining uncombined was recoverable by filtration and simple evaporation from the silica. Zinc oxide,² iron oxide,³ sand,⁴ manganese dioxide,⁵ lime,⁶ nickel or cobalt oxides,⁷ flint,⁸ alumina,⁹ with cal-

1. E. P. 932, 1861.

2. J. Webster, E. P. 2607, 1861.

3. L. Mond, E. P. 2556, 1862.

4. H. Baker, J. Poole and W. Stace, E. P. 2026, 1866.

5. E. Prentice, E. P. 1811, 1874.

6. W. Garroway, E. P. 7412, 1894; 2466, 1895; abst. Mon. Sci. 1896, **48**, 24; Chem. Ztg. 1895, **19**, 1735.

7. R. Main and W. Donald, E. P. 23819, 1895; abst. Jahr. Chem. 1897, **50**, 563; Chem. Ztg. 1897, **21**, 399; Mon. Sci. 1897, **50**, 165.

8. W. Garroway, E. P. 2489, 1896; D. R. 79699; abst. Mon. Sci. 1895, **46**, 120; Ber. 1895, **28**, 483; Chem. Centr. 1895, **66**, I, 982; Jahr. Chem. 1895, **48**, 723; Zts. ang. Chem. 1895, **8**, 112.

9. Soc. Anon. des Poudres et Nitrates, E. P. 14357, 1914; abst. C. A. 1915, **9**, 3338; J. C. I. 1915, **34**, 800. F. P. 473433; abst. Mon. Sci. 1916, **53**, 81.

cium carbonate, especially in a current of superheated steam or carbon dioxide¹ are some of the methods which have been proposed. J. Taylor² used uncalcined ferrous sulfate (copperas) or ferric sulfate (coquimbite); H. Baynes employed ferric oxide;³ while G. Lunge and F. Lyte⁴ prefer to use hematite, Venetian red being obtained as an additional by-product, a special form of patented retort⁵ having been constructed for the purpose. H. Blackmore proposes to produce nitric acid and peroxides at the same time, as by exposing barium nitrate to superheated steam, barium dioxide and nitric acid being formed.⁶

Other Nitric Acid Processes Using Metallic Nitrates. The method of J. White⁷ employs sulfuric acid and niter, and has for its object the prevention of the production of large quantities of weak nitric acid. The retort is charged with 1600 lbs. niter and 2000 lbs. "concentrated" vitriol, and distilled off in the usual manner, producing about 850 lbs. 96% HNO_3 and 210 lbs. of about 74%. In the next charge of the retort this weak nitric acid is added to the niter and vitriol, and when distilled is said to produce 1011 lbs. 96% HNO_3 and 210 lbs. of 74%. The reason why the weak acid is converted into stronger acid is appar-

1. A. Vogt, E. P. 22018, 1891; Chem. Centr. 1893, **64**, I, 806.

2. E. P. 4291, 1887; Chem. Centr. 1888, **59**, 880.

3. U. S. P. 632394, 1899; E. P. 7273, 1895. See also U. S. P. 481407, 1892; Jahr. Chem. 1897, **50**, 563; Mon. Sci. 1896, **48**, 168; Chem. Ztg. 1899, **23**, 804.

4. U. S. P. 514124, 1894. E. P. 13654, 1893.

5. D. R. P. 90654; abst. Chem. Centr. 1897, **68**, I, 1142; Chem. Ztg. 1897, **21**, 228; Jahr. Chem. 1897, **50**, 569; Wag. Jahr. 1897, **43**, 470; Zts. ang. Chem. 1897, **10**, 289. D. R. P. 74487. E. P. 7273, 1895; abst. Ber. 1894, **27**, 681; Chem. Centr. 1894, **65**, II, 262; Jahr. Chem. 1894, **47**, 532; 1897, **50**, 563, 569; Wag. Jahr. 1894, **40**, 477; Zts. ang. Chem. 1894, **7**, 271; Mon. Sci. 1896, **48**, 168; Chem. Ztg. 1899, **23**, 804. See also J. Vogel, Eng. and Min. J. 1900, 408.

6. U. S. P. 618772, 1899; 982466, 1911; abst. C. A. 1911, **5**, 1174. The process of Soc. Anon. des Poudres (E. P. 473433, 1914; abst. J. S. C. I. 1915, **34**, 551; J. S. C. I. Ann. Rept. 1916, **1**, 116) is for the production of alumina and nitric acid. Chem. Ztg. 1899, **23**, 150; Chem. Ztg. Rep. 1911, **35**, 129; Mon. Sci. 1899, **54**, 143; 1911, **75**, 113.

7. U. S. P. 648322, 1900; abst. Chem. Ztg. 1900, **24**, 425. Plisson, E. P. 19391, 1854; and addn. of June 25, 1855. Trainé & Hellmers, H. Wever and F. Brandenburg (D. R. P. 269656; abst. C. A. 1914, **8**, 2042; Mon. Sci. 1917, **84**, 35; Chem. Zentr. 1914, **85**, I, 712; Chem. Ztg. Rep. 1914, **38**, 103; Wag. Jahr. 1914, **60**, I, 355; Zts. ang. Chem. 1914, **27**, 134. Heat calcium nitrate. A. Schloesing, E. P. 441607; abst. J. S. C. I. 1910, **31**, 922. I. Grossmann, D. R. P. 160671; Chem. Zentr. 1905, **76**, I, 1548; Chem. Ztg. 1905, **29**, 571; Chem. Zts. 1906, **5**, 386; Jahr. Chem. 1905-1908, I, 1777; Wag. Jahr. 1905, **51**, I, 441; Zts. ang. Chem. 1905, **18**, 1151. J. Kessler, E. P. 5016, 1886.

ently that the excess of water combines with the niter cake. Whittaker's process¹ is similar.

The Oesterreichischer Verein² starts with ammonium nitrate (perhaps a preparation to take the place of niter during the war) and decomposes it with at least sufficient sulfuric acid to form ammonium hydrosulfate. In the production of nitric and hydrochloric acids,³ the nitric is produced in the usual manner by the action of sulfuric acid on NaNO_3 , and the NaHSO_4 thus produced mixed with an excess of salt and sufficient H_2SO_4 to produce Na_2SO_4 , the mixture being then heated in the HCl furnace.

The II. Frischer apparatus for nitric acid manufacture⁴ comprises a retort having a number of vapor discharge pipes arranged at different points and connected singly or in pairs to separate coolers, and joining together towards the end of the cooling system after most of the vapor has condensed. Or,⁵ the nitric acid may be made in a cylindrical bottom retort, in which the mass, by a revolving screw, is moved from the cold to the hot end. There are partitions arranged so that the gases can be separately carried off from every compartment and condensed. A. Campbell and A. Walker⁶ grind niter cake with niter and charge the mixture into retorts provided with mechanical agitators. The author has tried this process and was unable to make it work.

1. E. P. Appl. 15158, 1915; abst. J. S. C. I. 1916, **35**, 67.
2. D. R. P. 280967; abst. J. S. C. I. 1915, **34**, 491; Ann. Rept., J. S. C. I. 1916, **1**, 115; Mon. Sci. 1917, **84**, 77; Chem. Zentr. 1914, **85**, II, 175; Chem. Ztg. Rep. 1915, **39**, 2; Wag. Jahr. 1914, **60**, I, 356; Zts. ang. Chem. 1915, **28**, 21.
3. H. Howard, U. S. P. 1193552, 1916; abst. J. S. C. I. 1916, **35**, 962; C. A. 1916, **11**, 2391. See also W. Walker, E. P. 22853, 1894. H. Baker, U. S. P. 108090, 1870. J. Darling, U. S. P. 517001, 1894. W. Garraway, U. S. P. 590143, 1897; abst. Chem. Ztg. 1897, **21**, 821; Mon. Sci. 1898, **52**, 107.
4. E. P. 7099, 1915; abst. C. A. 1916, **10**, 2787; J. S. C. I. 1916, **35**, 537. See also W. Brookes, E. P. 2193, 1882. In the T. Banigan process (U. S. P. 1332195; abst. C. A. 1920, **14**, 1191) a mixture of pulverized niter cake and sodium nitrate is passed in a stream through a rotating tubular retort continuously while subjected to a tumbling movement. Near the discharge end of the stream a higher temperature is maintained than near the inlet end of the apparatus. Nitric acid produced is caused to flow in a direction opposite to the travel of the stream.
5. Chemische Produktenfabrik and G. Schuler, D. R. P. 261634; abst. C. A. 1913, **7**, 3397; Chem. Zentr. 1913, **84**, I, 523; Chem. Ztg. Rep. 1913, **37**, 420; Wag. Jahr. 1913, **59**, I, 435; Zts. ang. Chem. 1913, **26**, 477. See also J. Darling and H. Forrest, E. P. 5808, 1894.
6. E. P. 9872, 1894. See also Norsk Hydroelektrisk Kvaestof Aktieselskab., E. P. 8270, 1915; abst. J. S. C. I. 1916, **35**, 468; Chem. Ind. Ann. Rep. 1916, **1**, 116.

In order to obtain a residue easily fusible at the temperature of reaction which may be utilized for the preparation of HCl, Chatfield employs a large excess of vitriol for decomposing the nitrate. C. Claessen¹ briquettes the niter with a little vitriol and niter cake into cubes about an inch on a side.

H. Hemingway² mixes niter, vitriol and water, heating the mixture to 77° and gradually adding ferrous sulfate, ferric and sodium sulfates being obtained as by-products. Calcium nitrate produced from gypsum,³ lead nitrate,⁴ and manganic nitrate⁵ have been patented as basic material for the preparation of nitric acid by double decomposition with vitriol or in the case of manganesé, with water. In the process of W. Garroway,⁶ niter cake and niter are mixed in a retort and a spray of weak nitric acid is blown over the mixture by means of compressed air. The nitrogen oxides mixed with air and steam are regenerated into nitric acid by passing through towers and condensed. In the method as proposed by the Tentelew Chemical Works,⁷ com-

1. E. P. 6102, 1915; abst. J. S. C. I. 1915, **34**, 1009; Chem. Ind. Ann. Rep. 1916, **1**, 415; Mon. Sci. 1918, **85**, 17. D. R. P. 287795; abst. Chem. Zentr. 1917, **88**, I, 931; Chem. Ztg. Rep. 1915, **39**, 420; Zts. ang. Chem. 1915, **28**, 581.

2. U. S. P. 781826, 1905; abst. Chem. Zts. 1905, **4**, 269; Chem. Ztg. 1905, **29**, 223.

3. F. Schmidt, U. S. P. 928545, 1909. See also Chem. Werke vorm. H. Byk, E. P. 20366, 1908; abst. J. S. C. I. 1909, **28**, 982; C. A. 1910, **4**, 500. D. R. P. 208143; abst. C. A. 1909, **3**, 2042; Mon. Sci. 1912, **77**, 82; 1913, **79**, 65; Chem. Zentr. 1909, **80**, I, 1279; Chem. Ztg. Rep. 1909, **33**, 186; Chem. Zts. 1909, **8**, No. 1398; Jahr. Chem. 1909, **62**, I, 535; 1910, **63**, I, 586; Wag. Jahr. 1909, **55**, I, 424; Zts. ang. Chem. 1909, **22**, 748; Zts. Schiess. Spreng. 1909, **4**, 215. Aust. P. 41931, 1909. D. R. P. 217476, 1908; abst. Mon. Sci. 1913, **79**, 157; Chem. Zentr. 1910, **81**, I, 487; Chem. Ztg. Rep. 1910, **34**, 34; Chem. Zts. 1910, **9**, No. 1590; Jahr. Chem. 1910, **63**, I, 586; Wag. Jahr. 1910, **56**, I, 484; Zts. ang. Chem. 1910, **23**, 380; Zts. Schiess. Spreng. 1910, **5**, 53. Addn. to D. R. P. 208143; abst. C. A. 1910, **4**, 1227. Swiss P. 45368, 1909. Aust. P. 43492, 1912; addn. to Aust. P. 41931. F. P. 400305; abst. Mon. Sci. 1911, **75**, 148. D. R. P. 253467.

4. W. Mills, U. S. P. 755378, 1904; abst. Chem. Ztg. 1904, **28**, 363; Mon. Sci. 1904, **61**, 125. See A. Vogt and C. Wichmann, D. R. P. 69059; abst. Mon. Sci. 1894, **44**, 55, 923; Ber. 1893, **26**, 647; Chem. Centr. 1893, **64**, II, 508; Jahr. Chem. 1893, **46**, 447; Wag. Jahr. 1893, **39**, 422; Zts. ang. Chem. 1893, **6**, 358. K. Lieber and I. Walz; Wag. Jahr. 1869, **15**, 182; 1875, **21**, 381.

5. C. Schlarb, F. P. 422751, 1910; abst. C. A. 1912, **6**, 1968; Mon. Sci. 1913, **79**, 116; Chem. Ztg. Rep. 1911, **35**, 306.

6. E. P. 2466, 1895; abst. Chem. Ztg. 1896, **20**, 566; Mon. Sci. 1896, **48**, 24. E. P. 2489, 1896; 6777, 1899; abst. J. S. C. I. 1900, **19**, 349. See also C. Volney, J. S. C. I. 1901, **20**, 544, 1190.

7. E. P. 501637, 1916; abst. J. S. C. I. 1917, **36**, 1271. Chemische Werke vorm. H. Byk, Belg. P. 213650, 1909; Swiss P. 45318, 1909. The C. de Guide and David & Co. (Belg. P. 228121, 1910) process decomposes

mercial nitric acid is gradually added to a solution of zinc or nickel nitrate of such a concentration that it can be maintained at 126°-170° or even higher. The pure acid is said to immediately evaporate without decomposition, leaving the impurities (sulfuric acid and iron) in the solution, and is condensed.

Uebel Nitric Acid Process. C. Uebel and the Chemische Fabrik Rhenania¹ manufacture polysulfates as a substitute for sulfuric acid in the production of nitric acid from sodium nitrate, the polysulfates being prepared by heating acid alkali sulfate when mixed together with sulfuric acid. Schulz² in 1868 showed that a compound of bisulfate with sulfuric acid of the formula $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$ could be obtained by crystallization of sodium bisulfate in an excess of sulfuric acid, but no practical application of the process was made at that time. Polysulfates, thus obtained are, according to the patentee, a useful substitute for strong sulfuric acid in the formation of concentrated HNO_3 , in that a purer and more concentrated acid results, than where sulfuric acid alone is used. In the preparation of nitric acid by such polysulfates, there is formed a bisulfate which at the end of the operation may be withdrawn as a liquid, the residue being then re-converted into polysulfate by the addition of further amounts of sulfuric acid.

The apparatus, shown in Fig. 53 is so constructed, as indicated, that the decomposition of the niter is effected in two stages instead of one, the nitric acid in concentrated form being distilled from the mixture of nitrate and acid in the first stage, after which the process is completed by the distillation of a weaker acid in a separate retort, from the residue from the first distillation. For this purpose one or more retorts are charged with a mixture of niter and polysulfate or sulfuric acid, heated until the calcium nitrate by sulfuric acid. G. Masson, Belg. P. 200466, 1907; 205723, 1908. G. Glock, Belg. P. 149852, 1900. J. Price, Belg. P. 225335, 1911. F. Raynaud (Belg. P. 257580, 1913) treats aluminium nitrate with superheated steam and distills off the nitric acid formed.

1. E. P. 27240, 1898; abst. J. S. C. I. 1899, **18**, 372. U. S. P. 675760. D. R. P. 106962; abst. Mon. Sci. 1900, **56**, 117; Chem. Centr. 1900, **71**, 1, 636; Chem. Ztg. 1900, **24**, 80; Jahr. Chem. 1900, **53**, 239; Wag. Jahr. 1899, **45**, 407; Zts. ang. Chem. 1899, **12**, 1138. E. P. 3305, 1901; abst. J. S. C. I. 1902, **21**, 173. U. S. P. 681085; abst. Chem. Zts. 1902, **1**, 80; Mon. Sci. 1902, **58**, 8. D. R. P. 127617; abst. Mon. Sci. 1902, **58**, 152; Chem. Centr. 1902, **73**, 1, 286; Chem. Ztg. 1902, **26**, 73; Chem. Zts. 1902, **1**, 475; Jahr. Chem. 1902, **55**, 383; Wag. Jahr. 1902, **48**, 1, 359. Can. P. 153528, 1914.

2. Inaugural Dissertation, Berlin, 1868.

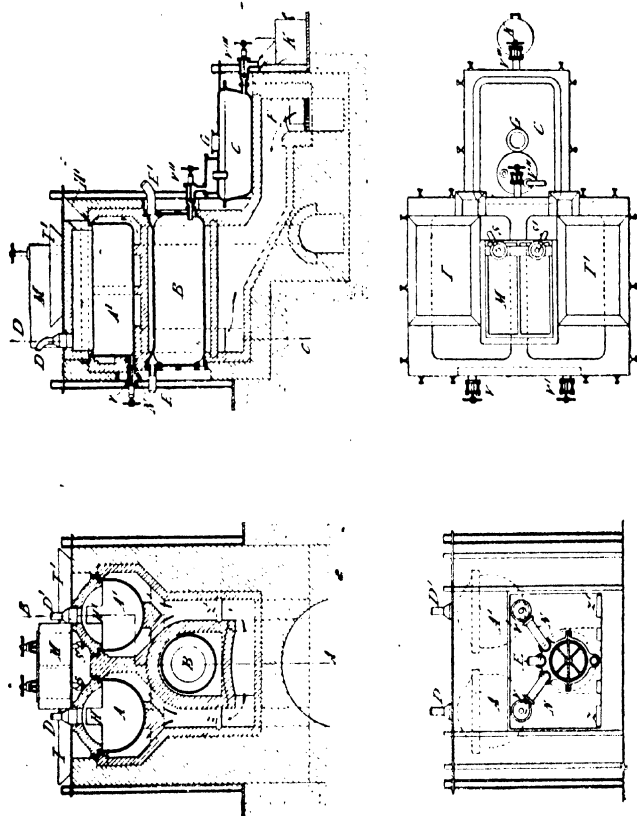


FIG. 53.—UEBEL PROCESS FOR NITRIC ACID MANUFACTURE

nitric acid has been expelled, when the residue in the retort is transferred to another retort containing hot bisulfate and heated to a sufficiently high temperature to expel the balance of the nitric acid.

For economy in working, two retorts may be set above a third retort in branch flues from the furnace heating the third (lower) retort, which is properly connected to the first two. The upper retorts are alternately charged and when the first stage in either is completed, the contents of that retort is run into the lower one by gravity, the lower draw-off cock being so placed that the residual sulfate contained therein is never entirely withdrawn, thus always leaving a quantity of hot bisulfate in the retort for the next operation.

More recently it has been found¹ that only half of the charge of nitrate is added to a full charge of vitriol, and the mixture heated to a low temperature (140°) so as to obtain an acid of highest concentration; the remainder of the charge of nitrate being then added and the temperature raised so as to completely distil off the nitric acid. The latter stage of the process may with advantage be conducted in two steps by first heating to 160°-170° to distil off the concentrated acid, and then raising the temperature to 250° or higher to remove the last portion of the acid. In the first phase of the process the niter and vitriol are gradually and simultaneously added, and controlled according to the progress of the action, the niter being also gradually introduced in the second stage of the operation.

• P. Claes has also² described the manufacture of polysulfates from niter cake and vitriol as a commercial article, while G. Glock³ endeavors to prevent the formation of bisulfate by feeding •

1. C. Uebel, U. S. P. 1141994, 1915. E. P. 19881, 1913. D. R. P. 261874, 277092; abst. C. A. 1913, **7**, 3398; Chem. Zentr. 1913, **84**, II, 463; 1914, **85**, II, 595; Chem. Ztg. Rep. 1913, **37**, 412; 1914, **38**, 479; Wag. Jahr. 1913, **59**, I, 435; 1914, **60**, I, 355; Zts. ang. Chem. 1913, **26**, 464; 1914, **27**, 565. F. P. 461452, 1915; abst. C. A. 1914, **8**, 2464; Chem. Ztg. Rep. 1914, **38**, 237. D. R. P. 210803; abst. Mon. Sci. 1912, **77**, 99; Chem. Zentr. 1909, **80**, II, 159; Chem. Ztg. Rep. 1909, **33**, 339; Chem. Zts. 1910, **9**, 1565; Jahr. Chem. 1909, **62**, 536; Wag. Jahr. 1909, **55**, I, 418; Zts. ang. Chem. 1909, **22**, 1468; Zts. Schiess. Spreng. 1909, **4**, 291. Belg. P. 259566, 1913; Aust. P. 65224. Swiss P. 67251; 1913. Swed. P. 38745.

2. E. P. 1072, 1900; abst. Chem. Ztg. 1901, **25**, 447. M. Hasenclever (J. S. C. I. 1911, **30**, 1293) has described in detail the Uebel apparatus, which treats 1800 kg. niter per 24 hours.

3. E. P. 18897, 1899. D. R. P. 110254; abst. Mon. Sci. 1900, **56**, 185; Chem. Centr. 1900, **71**, II, 228; Chem. Ztg. 1900, **24**, 316; Jahr. Chem. •

the H_2SO_4 , preferably heated to 100° – 130° , to the niter while the latter is heated to 120° . Atmospheric air is forced through the apparatus at the end of the process, only neutral sulfate remaining behind. Chemically the proposition does not appear feasible.

The Valentiner Vacuum Process for Making Nitric Acid.¹

This system of vacuum decomposition and distillation offers many obvious advantages, in that decomposition of the strong acid is greatly minimized by distillation under the diminished pressure while the time of distillation is also reduced, and the acid obtained contains a smaller proportion of dissolved oxides of nitrogen, and hence is more nearly colorless. The inconvenience to the workmen is not so apparent, for the leakage of fumes is much reduced, and a greater yield of purer and more concentrated nitric acid is claimed.²

In the original smaller Valentiner installation shown in Fig. 54 and the subsequent elaboration of the process as indicated in Figs. 59 and 60, the goose-neck (outlet pipe) from the still is connected to a small receiver, half filled with pumice stone or other absorbent not attacked by nitric acid and of a porous nature, so that any acid or solid spurting over mechanically from the still is retained. The vapors then next travel through two water-cooled condensers of stoneware coils arranged in series, and from thence through two separate sets of receivers. Here, by means of a three-way tap, the acid may be collected in a large receiver either at the commencement or at the close of the distillation process, while the more concentrated (95%–96%) nitric acid may be collected in separate receivers, from which any uncondensed vapors will pass into a reflux condenser comprizing an earthenware coil immersed in cold water. The vapors next pass through eight

1900, **53**, 240; Wag. Jahr. 1900, **46**, I, 393; Zts. ang. Chem. 1900, **13**, 373. Aust. P. 4205, 1901.

1. The Valentiner patents are, U. S. P. 920224. E. P. 610, 1892; 19192, 1895; 4254, 1907; abst. J. S. C. I. 1907, **26**, 1090. E. P. 374902; abst. Mon. Sci. 1908, **69**, 85; Chem. Ztg. Rep. 1907, **31**, 371. D. R. P. 63207, 88321, 144638; abst. Mon. Sci. 1896, **48**, 108; 1902, **58**, 24; Ber. 1892, **25**, 878; Chem. Zts. 1902, **1**, 14; Jahr. Chem. 1892, **45**, 2695; 1894, **47**, 2297; Wag. Jahr. 1892, **38**, 357; 1896, **42**, 406; Zts. ang. Chem. 1892, **5**, 526; 1896, **9**, 632. Aust. P. 36792. See also, Zts. ang. Chem. 1901, **14**, 161, 413, 495, 571, 658, 731. Fortieth Report British Alkali Works, 1903, 165; 1904, 157. Belg. P. 198121, 1907.

2. The first Valentiner patent is dated Sept. 8, 1891. G. Lunge had already called attention to the fact (Chem. Ztg. 1891, **15**, 167 (Mar. 15)) that nitric acid may be distilled in vacuum.

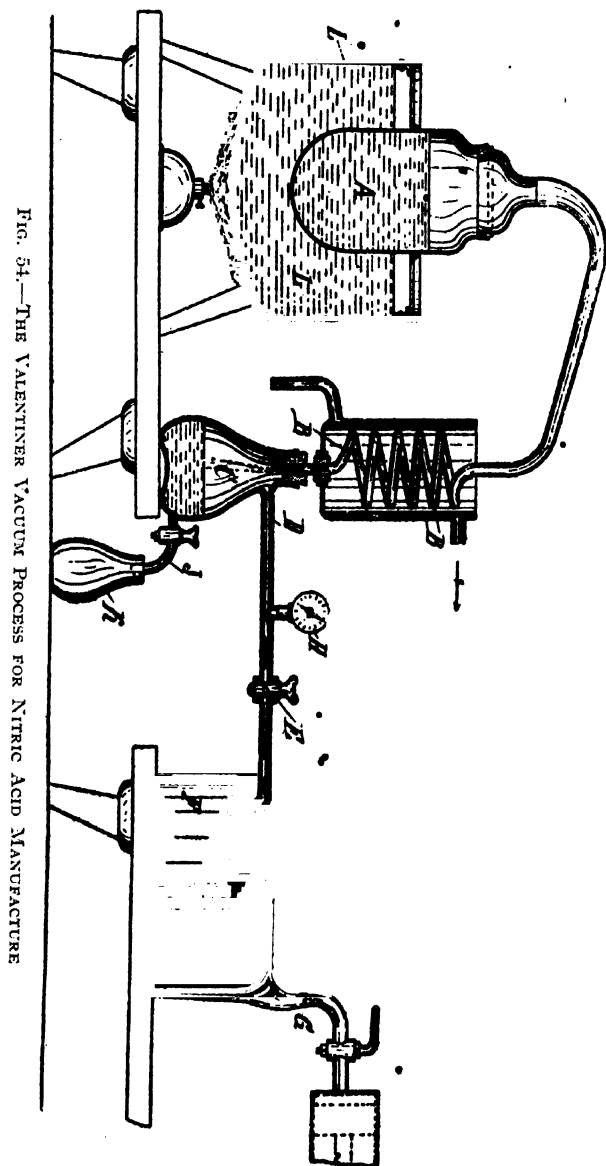
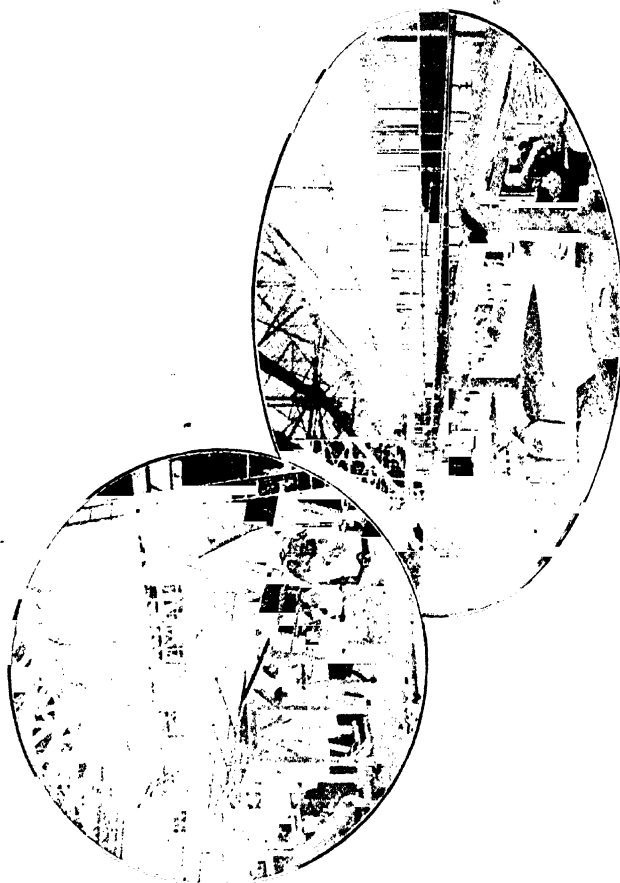
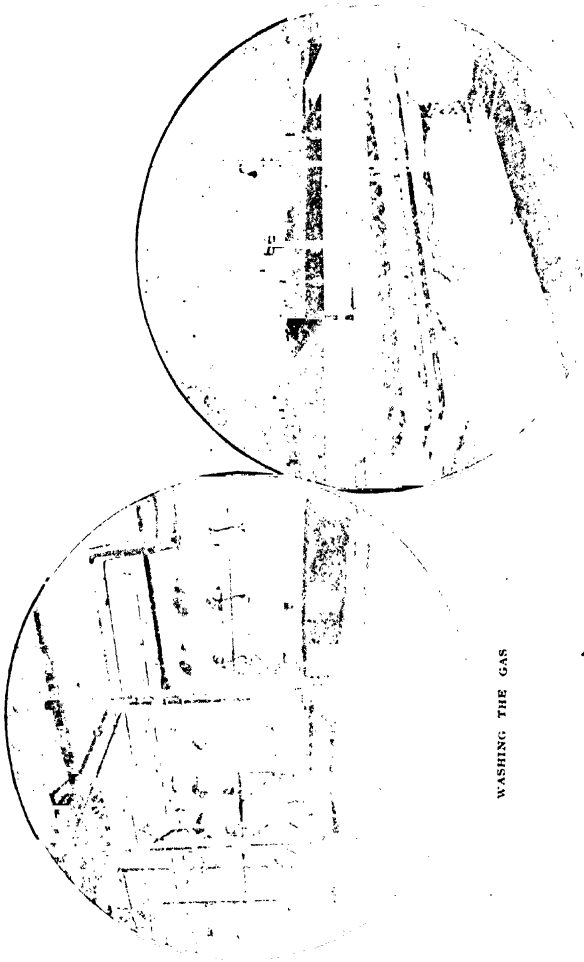


FIG. 54.—THE VALENTINER VACUUM PROCESS FOR NITRIC ACID MANUFACTURE



FIGS. 55 AND 56.—THE VALENTINER NITRIC ACID PROCESS



WASHING THE GAS

RESERVE ACID STOCK

FIGS. 57 AND 58.—THE VALENTINER NITRIC ACID PROCESS

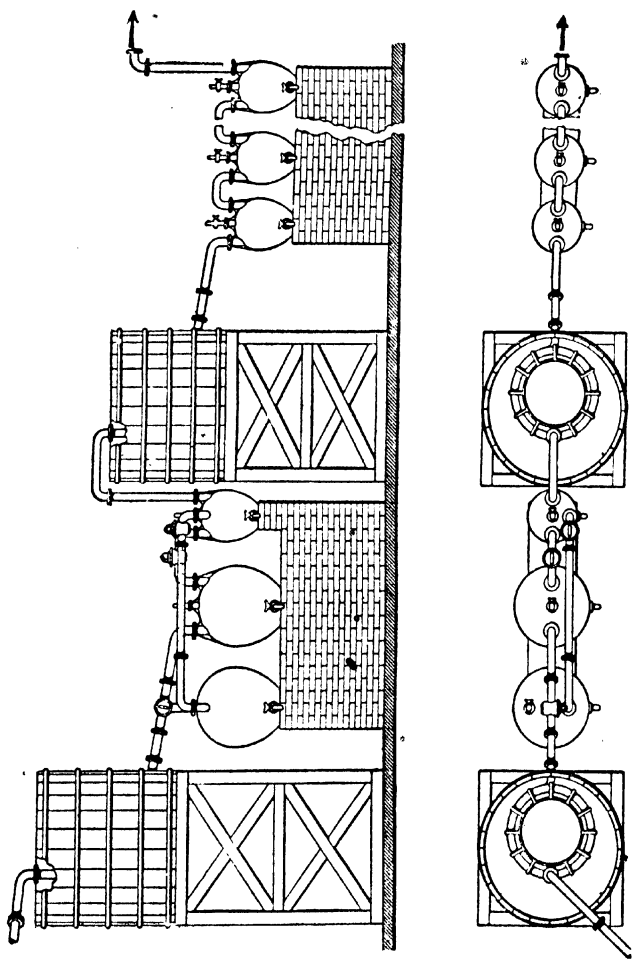


FIG. 59.—THE VALENTINER VACUUM PROCESS FOR NITRIC ACID MANUFACTURE

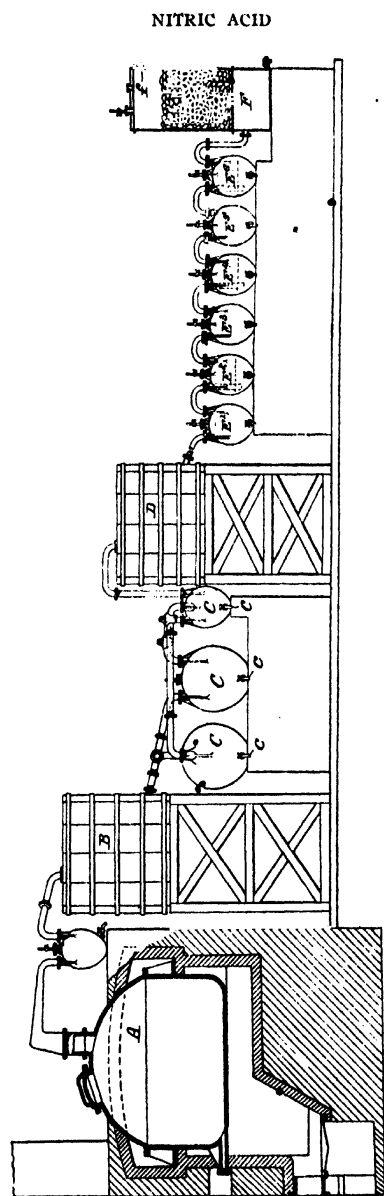


FIG. 60.—THE VALENTINER VACUUM PROCESS FOR NITRIC ACID MANUFACTURE

receivers, alternately empty and partly filled with water, and then seven more receivers alternately empty and partly filled with milk of lime to remove any traces of nitrous gas. The system ends by connection to a vacuum pump. The patentee claims¹ that by means of this process it is possible to convert all dilute acid obtained by any method and which, owing to its low degree of concentration is difficult to utilize. If, for instance, a mixture of 800 kilos H_2SO_4 with 1200 kilos HNO_3 of sp. gr. 1.40 is subjected to distillation in partial vacuum in the Valentiner process, the temperature need not rise above 100° , whereby the major portion of the water will be retained by the sulfuric acid while nitric acid of 94%–95% monohydrate will distil over and collect in the receivers.

The passage between the retort and the condensing coil is restricted to half the diameter of that coil, the result being that the higher pressure maintained in the retort prevents the tendency to spurt of sodium nitrate through the sulfuric acid, and therefore tends to increase the speed of distillation. The condenser extends to the bottom of the first receiver so as to form a liquid seal for the pure nitric acid to be retained while the HCl and the nitrogen oxides pass on.

According to P. Hallwell,² the cast iron retort is nearly round and holds about 1750 pounds of nitrate of soda per charge. It is surrounded by hot gases rather than being directly heated by a flame. The top of the retort has openings for charging the nitrate, for the admission of air, for discharging the acid vapors, for introducing the sulfuric acid and for the introduction of a thermometer. The goose-neck which carries away the acid vapors is 8 inches wide, the vapors being first led into a glass cylinder that they may be observed, and from thence into an earthenware bend connected with an earthenware worm of $2\frac{1}{2}$ inches internal diameter.

When the nitrate has been charged in, all necks are closed, the vacuum pump is started, and by opening a valve in the sulfuric acid connecting system, the vitriol is sucked into the retort. Much gas is disengaged at once, nitrosyl chloride being formed which travels no farther than the receivers behind the second

1. E. P. 13826, 1895; abstr. *Jahr. Chem.* 1897, **50**, 563.

2. *Chem. Ztg.* 1895, **19**, 118.

worm. When the vacuum indicates 500 mm. mercury, the fire is started, and the temperature rises to 80°, which temperature is maintained during the first stage. The vacuum fluctuates between 650°-670 mm. Hg, the temperature at the close of the process being driven to 120°-150°. When practically no more acid distils over the temperature is again raised to 170°-180° in order to increase the limpidity and fluidity of the niter cake so it will more quickly flow out of the retort.

As the result of the comparatively low temperature, the decomposition of the nitric acid and the wear on the iron is kept at a minimum, while the yield is mostly strong acid, and nearly to theory in quantity. With undried niter and sulfuric acid of 142° Tw. the yield is 95.7% on the theory, this comprizing 3.8% impure acid of 21½° Tw. and the balance up to 99.5% of the theory comprizing 78% nitric acid. With undried nitrate and 160° Tw. vitriol, the yield is 99% HNO₃ of 81% and 0.8% as dilute nitric acid.

According to Hallwell, a charge requires but 7-8 hours to run off, so that two charges may easily be run in 24 hours, the fuel consumption being 8-9 parts of coal for firing, and 6-7 parts for the vacuum, or a total of 14-16 parts to 100 of niter, as against 32-35 parts in the older processes. There is no steam or compressed air required for refining.

The temperature of the first receiver is but 35°-40°, the rear receivers being cold. The receivers are made extra heavy and practically globular to guard against their collapse from atmospheric pressure when the vacuum is applied. Any crack in the pipes is remedied by the application of a cement composed of asbestos and silicate of soda. When undue frothing is noted, it is remedied by opening the air-valve.

The total ground dimensions of the apparatus is 40 by 17 feet, the width of the condensing portion only 5 feet. The action of the escaping acid gases must be prevented from coming in contact with the air pump by charging the receiver with milk of lime as above described. S. Dreyfus¹ has patented a new means for packing the pistons of nitric acid vacuum pumps.

K. Francke² has also communicated observations on the

1. E. P. 42527, 1916; abst. J. S. C. I. 1917, **36**, 201.
2. Chem. Ztg. 1897, **21**, 511; abst. J. S. C. I. 1899, **18**, 492; Chem. Centr. 1897, **68**, 11, 438; 1899, **70**, 1, 952; 11, 575.

Valentiner process, in which it appears that for each ton of niter decomposed there is required about 87 cu. ft. condensing space. It is also important that the retorts should be entirely surrounded by the fire and that their upper parts and the branch pipe should be protected by acid-proof lining. Where the condensing area is sufficient and the cooling efficient, the niter cake is free from nitrogen compounds, and the first receiver which is filled with water is only changed once after several operations. Theoretically 1000 k. 96% niter with 2% water should yield 796.5 k. HNO_3 sp. gr. 1.486 (89.3% HNO_3), while from 1000 k. 96% niter previously dried, 771.5 k. nitric acid sp. gr. 1.497 (92.2% HNO_3) is obtainable, and in practical working, the yield actually obtained is but little less. With concentrated acid, however, there is liable to be considerable frothing due to the production of NO_2 , because it requires some time for the acid to thoroughly permeate the niter; this, however, may be avoided by employing more vitriol, or by introducing liquid nitric acid into the retort.

Bergmann has also favorably reported on this process,¹ but finds it necessary to retain the nitrosyl chloride by passing through milk of lime as described in order to properly protect the vacuum pumps. According to his figures, each 16 tons of nitrate decomposed required 5 tons of coal for fuel.

Inoue² prefers this process to that of Guttman, both from financial and sanitary viewpoint. He finds that when the retort is well cooled, at a temperature of 150° , a smaller yield of nitric acid is obtained at the commencement of the process, but of high concentration (98.2%), and at 180° , a concentration of 97.95% is obtainable.

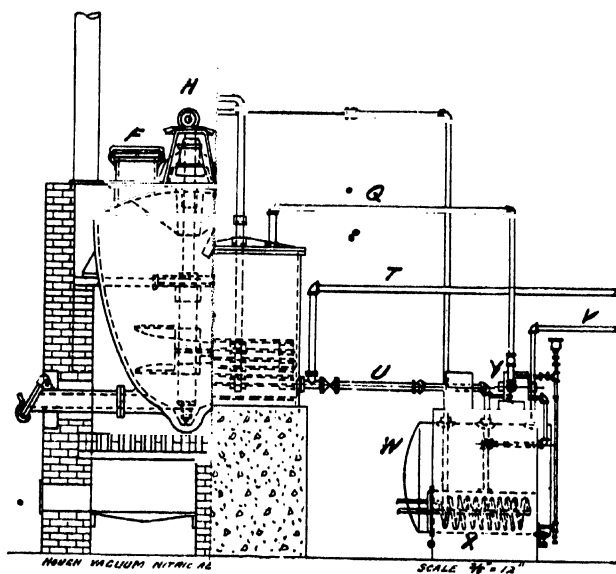
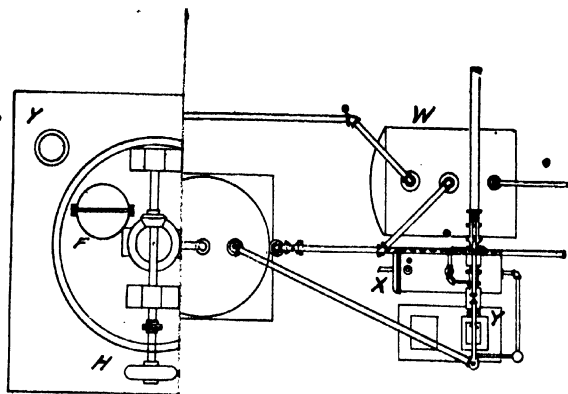
The vacuum process of C. Dreyfus³ is similar. In order to obtain a practically theoretical yield of nitric acid from niter certain conditions of temperature are employed, which will enable substantially the whole of the nitric acid to be obtained, but will hold back the impurities from contamination with the acid. The method of C. Volz⁴ is a vacuum process for nitric acid

1. Zts. ang. Chem. 1899, **12**, 1003; abst. J. S. C. I. 1899, **18**, 1122; Jahr. Chem. 1899, **52**, 470.

2. Chem. Ztg. Rep. 1914, **38**, 399.

3. E. P. 13826, 1895; abst. Jahr. Chem. 1897, **50**, 563.

4. U. S. P. 500785, 500786, 1893. D. R. P. 63207; abst. Mon. Sci. 1896, **48**, 108; 1902, **58**, 24; Ber. 1892, **25**, 878; Chem. Zts. 1902, **1**, 14; Jahr. Chem. 1892, **45**, 2695; 1894, **47**, 2297; Wag. Jahr. 1892, **38**, 357; Zts. ang. Chem. 1892, **5**, 526.



manufacture, and is similar to that of Valentiner.

F. de Jahn decomposes niter with sulfuric acid under diminished pressure at lower temperatures,¹ by constantly agitating and avoiding fusion of the bisulfate formed. The temperature is to be kept below 384° F.

Hough Nitric Acid System.—In the United States and Canada during the war so recently ended, a number of plants have been installed for the manufacture of nitric acid according to principles designed by A. Hough, which present many novel and interesting features. The plant, which is shown in Figs. 61 and 62, consists of a cast iron still provided with an agitator, suitable stuffing box, cast iron shaft, driving gears, and the necessary arrangements for filling the still with niter and vitriol and the removal of the niter cake.²

A condensing system is provided of ample cooling surface and sufficient length of cooling members to ensure the complete liquefaction of the nitric acid vapors, the terminal of this system being connected with a sulfuric acid-containing scrubber, which in turn is connected with a Nash vacuum pump (see Fig. 63), the piston of which consists of sulfuric acid. The heat generated by the action of the vacuum pump is absorbed in a cooling device, the sulfuric acid constituting the piston of the pump automatically, circulating through a tank provided with a cooling coil. By this means the pump is maintained at substantially constant temperature.

In the operation of the unit, the agitator in the still is started, and the niter charge introduced through the opening *F*, after which the cover is closed. An amount of sulfuric acid of the desired strength is measured out in the scrubber tank *S*—this constituting the acid charge of the still—the acid being dropped into the tank *W* through the pipe *U*. The cock on *U* is now closed, and a second charge of vitriol run into *S*.

The pump *Y* is now provided with about 4000 lb. H_2SO_4

1. U. S. P. 1023133, 1023138. D. R. P. 252374. Abst. C. A. 1912, **6**, 1662; 1913, **7**, 224, 873; Chem. Zentr. 1912, **83**, 11, 1707; Chem. Ztg. Rep. 1912, **36**, 390, 663; Wag. Jahr. 1912, **58**, 1, 421; Zts. ang. Chem. 1912, **25**, 2377; Zts. Schiess. Spreng. 1912, **7**, 454; Mon. Sci. 1912, **77**, 132. See also F. de Jahn, U. S. P. 1141948, 1143366, 1151537, 1159364, 1159365; abst. J. S. C. I. 1915, **34**, 799, 833, 1249; Chem. Ztg. Rep. 1916, **40**, 413, 429; 1917, **41**, 171.

2. U. S. P. 1312118, 1326267, 1918.

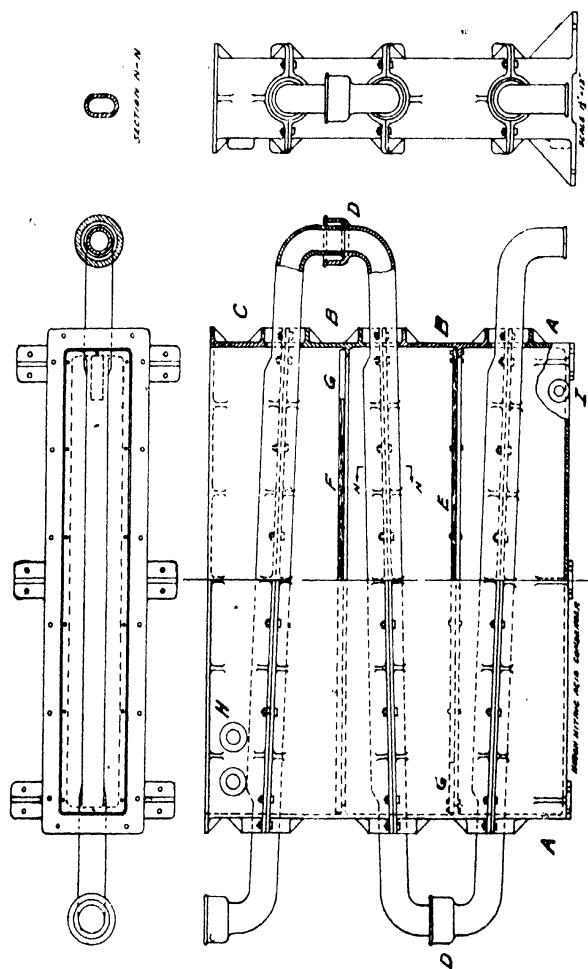


FIG. 62—THE HOUGH NITRIC ACID CONDENSER

(of about 94% monohydrate), by introducing the acid into the tank *X*, which is fitted with a cooling coil, the pump being then started. As the vacuum develops in the system, the sulfuric acid is drawn from *W* by means of the pipe *P*, into the still *A*, being distributed over the surface of the niter by means of the annular trough *C*. At this period a large quantity of strong nitric acid will be generated and condensed, flowing through the hydrometer arrangement, and ultimately into the receivers, *R*₁ and *R*₂, the latter being equipped with gauge glasses, by means of which the quantity of nitric acid is continually under observation.

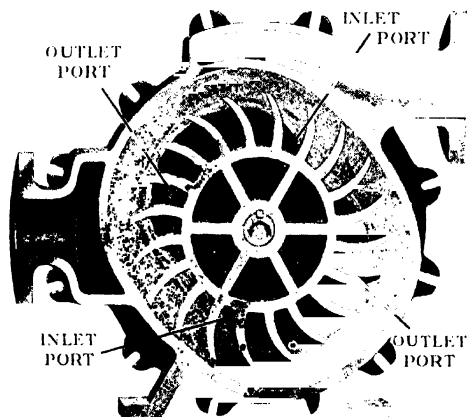


FIG. 63.—THE NASH VACUUM ACID PUMP

The drawings show the nitric acid plant as equipped with a bleacher, and the necessary cooling system to condense and cool the acid before it enters the receivers. This bleacher is only necessary when the nitric acid is required practically free from chlorine and nitrogen oxides, the acid made without the bleacher, seldom carrying over 0.1% lower nitrogen oxides.

It will be apparent, therefore, that the distillation commences with a small amount of sulfuric acid in the still, which amount increases as distillation progresses. This results in a uniform curve of distillation, and the mass in the still maintains a homogeneous condition, induced by the continual agitation. The introduction of the charge of sulfuric acid to the still requires about

an hour, during which time from half to two-thirds of the distillate has passed over, leaving the balance to distill in about two hours additional, the total distillation run being, therefore, not to exceed 3 hours operating normally.

The niter charge is 5000 lb. to 5100 lb. Sulfuric acid, the total blend of nitric acid obtained averaging 92% HNO_3 . When the sp. gr. of the distillate falls too low, the cocks communicating with the receivers R_1 and R_2 are closed, and the weak nitric acid by-passed into a suitable container. At this point the temperature of the still is raised to increase the fluidity of the niter cake before discharging.

After the latter has been run off, the still is again charged with niter. The sulfuric acid in the scrubber S is dropped into W , and a fresh lot of sulfuric acid put in the scrubber, the Nash pump being then started. A slightly different condition now exists, as the sulfuric acid from the scrubber contains about 3% HNO_3 obtained by absorption from the previous run. This goes into the still as so much sulfuric acid, and assists in the ease of reaction, it being well known that a small amount of nitric acid admixed with the sulfuric, is desirable. The capacity of the condenser and scrubber is so adjusted that substantially the entire amount of nitric acid generated is recovered, there being no issuance of nitric vapors from the Nash pump.

This new type of vacuum nitric system eliminates the major portion of the troubles and expensive up-keep of many of the systems heretofore proposed, especially those which included the old-fashioned reciprocating pump with bronze cylinder linings and lignum vitae pistons. The troublesome absorption pots are also dispensed with, as it is immaterial if a little nitric acid gets through to the pump, for it is instantly absorbed by the sulfuric acid acting as the piston, and so, in the course of time, this acid is used in the still, and therefore is ultimately utilized.

Every portion of the system subjected to contact with acid vapor is made of high silicon metal, no earthenware being used, while the hydrometers and glass parts are of Pyrex. Depreciation of the metal in the Nash pump is said to be exceedingly slight, as the gases are dry from the sulfuric acid dehydration.

When the bleacher is employed in the system, the spray method of cooling the condenser pipes is employed, as the hottest

portion of the condenser is at the bottom. When operating without the bleacher, the condenser is cooled by introducing the water at the bottom of the housing, where it zig-zags upwards between the wood diaphragms, the hottest part of the condenser being at the top.

The claims made for this system by the manufacturers (Buffalo Foundry & Machine Co.) are:

1. Output capacity is much greater than any other system hitherto suggested, because eight charges may normally be run off per 24-hour day.
2. Output of nitric acid per capital investment is greater than with other systems.
3. Nitric acid obtained is of higher average HNO_3 content, and is of a greater degree of purity, the actual net yield of nitric acid being also higher.
4. Plant depreciation is unusually low, owing to the low temperature required to effect distillation, by virtue of the high vacuum employed in the nitric still.
5. Frothing in the still does not occur, this being prevented by agitation of the charge, the method of introducing the vitriol, and the fact that a third of the nitric has passed over by the time all sulfuric has been introduced.

In the above process, particular attention is directed to the fact that the nitric vapors enter the base of the bleacher *I*, then upwards into the condenser *J*, the hot vapors meeting the refluxing nitric, which trickles down through the perforated plates in the bleacher, and deprives the condensed nitric of chlorine and the lower nitrogen oxides, by means of the low solubility in hot nitric acid.

The bleached hot nitric runs through the coolers *L*, thence through the hydrometer equipment *M*, the temperature and gravity of the acid being at all times observable by means of the hydrometer and thermometer shown at *N*. The vacuum pump is connected with the scrubber by means of the pipe *Q*, while the pipe *T* communicates with the source of sulfuric acid supply, all as shown in the drawing herein.

- An important part of this plant, is the Hough condenser for the nitric acid, which consists of a set of high silicon, metal S-pipes fitted into a housing of cast iron, having diaphragms of •

heat non-conducting material placed between the condensing pipes so as to ensure a zig-zag flow of the cooling water around the pipes, in true countercurrent principle.

In ordinary practice, the nitric vapors enter at the top of the condenser, and condense as they pass through the pipes, the cooling water entering the bottom of the housing, passing upwards, following the line of the pipes, and passing at alternate ends of the housing through the ports provided at each end of the wooden diaphragm.

The condenser pipes are oval where they are immersed in the cooling water, but round where they project through the housing. This shape of pipe gives maximum condensing effect, and renders the mounting very simple and efficient from a mechanical viewpoint. The bell joints *D* are caulked with lead wool to a solid mass. The water joints between the pipes and the housing are packed with oakum or similar material. This type of condenser is slightly modified where it is to be used on the water spray system, and when only muddy water is available, the sides of the housing being made readily removable, to expose the pipes for cleaning purposes.

The Griesheim Nitric Acid Plant.¹ This system has been used extensively in Germany and with satisfactory results, both as to yields and quality of nitric acid produced, and low upkeep. The general arrangement of a typical Griesheim plant is indicated in Fig. 64, in which the nitric acid, distilling out of the usual retort *A* passes first into a tourelle *B* for intercepting niter during possible foaming, then into an earthenware condenser *E*, immersed in cold water or in brine. Uncondensed vapors pass from *E* into *C D* through *F*, and finally into the usual tower *G*, where the vapors meet a fine stream of water passing over coke, broken brick or other refractory material.

At the commencement of the process a concentrated acid distills over contaminated with HCl, nitrosyl chloride and other chlorine-containing bodies, the next fraction being the main portion of the distillate, but tinged with nitrogen oxides. A blast

1. Chemische Fabrik Griesheim Elektron, D. R. P. 170532; abst. Mon. Sci. 1907, **67**, 145; Belg. P. 187592, 1905; E. P. 891, 1901; 19986, 1905; abst. J. S. C. I. 1906, **25**, 696. J. Lang, U. S. P. 477375, 1892. Chem. Centr. 1906, **77**, 11, 185; Chem. Ztg. 1906, **30**, 562; Chem. Zts. 1907, **6**, 19; Jahr. Chem. 1905-1908, I, 1793; Wag. Jahr. 1906, **52**, I, 445; Zts. ang. Chem. 1907, **20**, 972; Zts. Schiess. Spreng. 1906, **1**, 189.

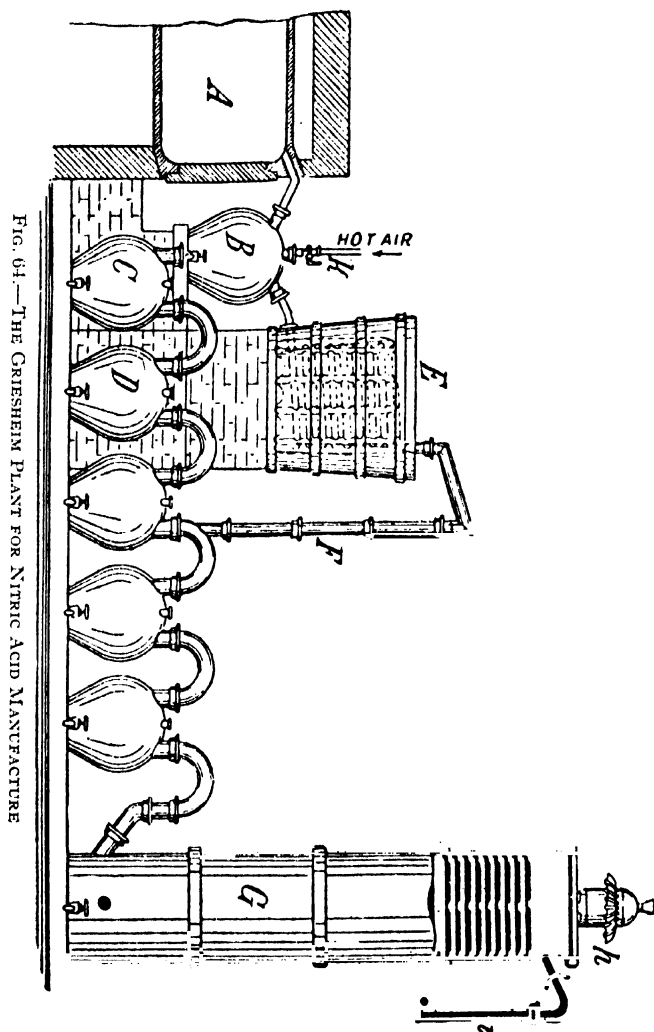


FIG. 64.—THE GRIESHEIM PLANT FOR NITRIC ACID MANUFACTURE

of hot air may be introduced at *K* into the receiver *B* to remove this color, which also tends to remove the volatile chlorine compounds. By adjustment of the temperature of the water in the condenser *E*, it is possible within rather narrow limits to regulate the quality and purity of nitric acid passing through.

Fig. 64 shows a "Griesheim" condensing system, much used in Germany. Here the nitric acid, distilling out of retort *A*, passes first into *B* and then into an earthenware condensing coil *E*, standing in cold water. The vapors then pass through the pipe *F*, through a series of earthenware receivers, and then into the plate column condensing tower *G*.

First of all, at the lowest temperature the strongest acid distils over, contaminated, however, by HCl , NO_2Cl , and similar chlorine-containing volatile compounds. Next, there distils over the main quantity of strong acid, fairly pure, but contaminated with red nitrous fumes. To oxidize these a stream of hot air is blown in at *K*.

In some forms of apparatus (e. g., Oscar Guttman's) the oxidation is automatically effected by causing the gases coming from the still to pass into an enlargement in the pipe, where they produce an injector action and suck in a quantity of air through perforations in the socket pipe, thus causing oxidation of the nitrous to nitric acid.

The air not only purifies the condensed nitric acid from nitrous acid, but also frees it from volatile chlorine compounds, such as NO_2Cl . By regulating the temperature of the water in which the cooling coil *E* (Fig. 64) is immersed, the quality of the acid collecting in *B* can also be regulated to some extent, and the acid can be withdrawn in successive fractions as it comes over into the receiver *C*. In the tower *G* (Fig. 64) all the nitrous fumes finally escaping condensation are absorbed by the down-streaming water, so as to form a dilute nitric acid of 1.35-1.36 sp. gr. The water enters at *H*.

Condensation of Nitric Acid. While the condensation of nitric acid is merely a cooling process, it is preferably so regulated and manipulated that the stronger and weaker acids which distil over at different stages of the process, are collected separately. For many years only air cooling was employed, which has a much decreased efficiency as compared to the methods of water cooling

now universally used. The latter is also much less expensive.

The older nitric acid condensing systems comprized a number of earthenware receivers which were, in reality, large Woulff bottles, and these were arranged in series of twenty or more, according to the capacity of the retort and the speed of distillation. H. Goebel¹ appears to have been the first to propose the cooling of nitric acid vapors by means of water, employing for this purpose a long glass tube placed in a trough. A. Trobridge² protects earthenware pipes used in the manufacture of nitric acid from breaking with cold water by surrounding the earthenware pipe with a pipe of lead. W. Ostwald³ uses nickel steel pipes, but nickel resists nitrogen oxides only in the gaseous form. D. Donnachie⁴ uses a nitric acid condenser comprizing sets of perpendicular pipes, water-cooled, while W. Hof⁵ makes use of inclined tubes of quartz glass or zirconium glass. M. Leblanc⁶ passes the vapors through tubes cooled both inside and outside by means of concentric pipes, the apparatus of A. Hough⁷ being similar.

The nitric acid condenser of F. Moore and J. Hall⁸ comprizes a number of cooled tubes between which the vapors, entering by a pipe, pass upwards in such a manner that the resulting liquid, flowing downwards, is heated by the upflowing vapor, thus obviating the absorption of nitrogen oxides. Further intimate contact

1. Dingt. Poly. 1876, **220**, 241; abst. Chem. Tech. Rep. 1876, **15**, I, 403; Jahr. Chem. 1876, **29**, 1090.

2. E. P. 25435, 1906; J. S. C. I. 1907, **26**, 1278. A. Cocking (E. P. 130038, 1918; abst. C. A. 1920, **14**, 210) treats dilute nitric acid with ammonia, and the solution of ammonium nitrate evaporated to crystallization, which are then heated with an excess of strong sulfuric acid under reduced pressure to obtain concentrated nitric acid and NH_4HSO_4 . The residue is treated with ammonia to obtain neutral ammonium sulfate. Cf. E. P. 125444, 129305; abst. C. A. 1919, **13**, 2258, 2978.

3. D. R. P. 207154; abst. Chem. Zentr. 1909, **80**, I, 1127; Chem. Ztg. Rep. 1909, **33**, 145; Jahr. Chem. 1909, **62**, 531; Wag. Jahr. 1909, **55**, I, 415; Zts. ang. Chem. 1909, **22**, 645; Zts. Schiess. Spreng. 1909, **4**, 108.

4. Chem. Trade J. 1904, **35**, 380; abst. J. S. C. I. 1904, **23**, 983.

5. U. S. P. 1099368. D. R. P. 279121; abst. C. A. 1914, **8**, 3101; Mon. Sci. 1914, **81**, 138. F. P. 463208, 1913; abst. J. S. C. I. 1914, **33**, 421. E. P. 21291, 1913; abst. J. S. C. I. 1914, **33**, 646.

6. F. P. 462712; abst. Chem. Ztg. Rep. 1914, **38**, 419. See E. I. Du Pont de Nemours Co., E. P. 135535, 1919. U. S. P. 1292948, 1919. Abst. J. S. C. I. 1919, **38**, 285-A; 1920, **39**, 64-A.

7. E. P. 101307, 1916; abst. C. A. 1917, **11**, 88; J. S. C. I. 1916, **35**, 1108.

8. E. P. 28892, 1910; abst. C. A. 1912, **6**, 1506; J. S. C. I. 1911, **30**, 1117; Chem. Ztg. Rep. 1912, **36**, 287. Hall, E. P. Appl. 14588, 1915; abst. J. S. C. I. 1916, **35**, 64.

of the vapor with the hot vapors is effected in a chamber formed of perforated partitions and packed with broken pumice. In another process,¹ the weak nitric acid first distilling by itself is collected, and is added to the next charge of nitrate and vitriol. The process of A. Charles and F. Lancaster² is analogous.

Berl and Innes³ employ tetraeders of aluminium wire gauze as fillers for absorption towers. For the absorption of alkaline liquids in order to produce nitrites, iron wire is used. In the absorption of nitrous gases in water for the production of nitric acid according to the process of F. Haussner,⁴ there is interposed between each absorption chamber small vessels arranged one upon the other for oxidizing. I. Moscicki⁵ constructs an absorption chamber shaped as a right angle with several perpendicular, sieve-holed diaphragms, in which the small compartments thus formed are filled with pieces of glass or quartz, the gas passing horizontally through the diaphragm perforations while the compartments are systematically rinsed with compressed air in order to produce an acid of high concentration. In securing a quiet and uniform distillation in nitric acid manufacture,⁶ the nitrate before charging into the retorts is pressed into cubes with vitriol and bisulfate from a previous operation. The complicated acid-collecting apparatus of E. Keller,⁷ combines a plurality of towers, the absorbing arrangement being substantially automatic. The W. Bate and F. Orme condenser⁸ comprizes an earthenware stack arranged vertically in a wooden frame, the pipes being connected to each other in pairs at the top by means of bends. Open topped water jackets surround the pipes, an unusually large condensing surface being obtained. In this respect the condensing unit of F. Nathan

1. J. White, U. S. P. 648322; abst. Chem. Ztg. 1900, **24**, 425. See also D. Plisson, E. P. 988, 1854.

2. E. P. 107255, 1916; abst. J. S. C. I. 1917, **36**, 962.

3. In this connection see H. Weidig and R. Remmey, E. P. 1082, 1888; abst. Mon. Sci. 1908, **69**, 105.

4. E. P. 7419, 1914; abst. J. S. C. I. 1915, **34**, 800; E. P. 469649, 1914; abst. J. S. C. I. 1915, **34**, 80.

5. U. S. P. 1046212, 1097870; abst. C. A. 1913, **7**, 563; 1914, **8**, 2509; Chem. Ztg. Rep. 1913, **37**, 190.

6. C. Claessen, D. R. P. 287795, 1914; abst. C. A. 1916, **10**, 2029; Chem. Zentr. 1917, **88**, I, 931; Chem. Ztg. Rep. 1915, **39**, 420; Zts. ang. Chem. 1915, **28**, 581.

7. U. S. P. 1247280, 1917; abst. J. S. C. I. 1918, **37**, 56-A.

8. E. P. 25790, 1902; abst. J. S. C. I. 1903, **22**, 212. J. Graham, E. P. 6051, 1902; J. S. C. I. 1903, **22**, 907.

and J. and W. Thomson¹ is quite similar. Aluminium² and cobalt-nickel alloy containing 4% of silver³ have been advocated for cooling, condensing and transportation of nitric acid.

L. Rohrmann and H. Niedenführ⁴ prepare nitric acid as shown in Fig. 65 by distillation in a retort *k*, and the gases evolved are

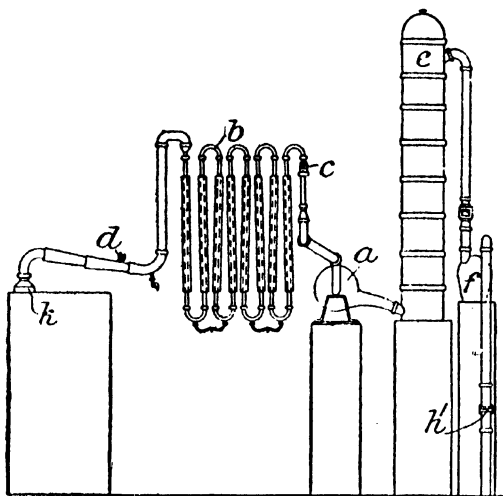


FIG. 65.—THE NIEDENFÜHR NITRIC ACID PLANT

passed through a condenser *b*, whereby the nitric acid is absorbed. The unabsorbed nitrous fumes are withdrawn by a fan, ventilator, or the like, *a*, between which and the condenser is an inlet *c* for additional air for oxidizing the fumes. A small amount of air may be also introduced at the usual place, namely at *d*. The mixed gases then pass to further condensing plant or "tail-apparatus" *e, f*, wherein further quantities of nitric acid are absorbed. This tail-apparatus may consist of two absorbing or plate columns such as *e*, in the first of which a concentrated solution of nitric acid is obtained by charging the column with a limited

1. F. P. 406806, 1909; abst. Chem. Ztg. Rep. 1910, **34**, 151.

2. Norsk. Hydro-Elektrisk Kvaelfstoftselskab, F. P. 451812; abst. Mon. Sci. 1914, **81**, 7. Can. P. 176626.

3. Gebrüder Borchers, Chem. Ztg. Rep. 1913, **37**, 87.

4. E. P. 29746, 1897; 4353, 1905; abst. J. S. C. I. 1905, **24**, 1012. See also H. Niedenführ, U. S. P. 798205, 1905; Belg. P. 182680, 1905.

quantity of liquid, and in the second a dilute solution is obtained by charging the column with an excess of liquid so as to absorb all the gases possible. The dilute acid from the second column is used as the absorbent in the first column. A damper or the like, h^1 , can be placed after the last part of the tail-apparatus so as to regulate the pressure and the speed of the gases.

The J. Sköglund nitric acid condenser,¹ is employed in many factories in the United States, being at the present time built of duriron or other high silica iron, and is shown in Fig. 66.

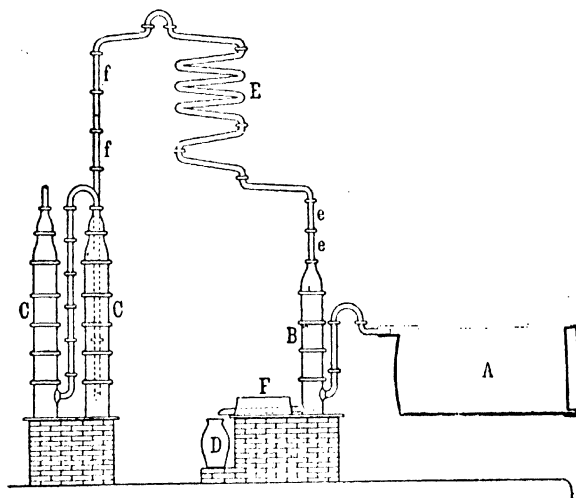


FIG. 66.—THE SKÖGLUND NITRIC ACID CONDENSER

The apparatus has also been described in detail by A. Otto² and by E. Wolff.³ By means of this apparatus pure nitric acid is obtained in a single operation, which requires little or no special treatment in order to remove the lower nitrogen oxides, containing 0.05% 0.15% N_2O_3 , and the strength is seldom under 94%. The "bleaching" and the removal of the nitrogen oxides

1. U. S. P. 591087, 1897; 603402; F. P. 271025; abst. Mon. Sci. 1895, **46**, 747. D. R. P. 104357, 105704; Belg. P. 131113, 1897; Swiss P. 32445, 1904. Mon. Sci. 1900, **56**, 13; abst. Chem. Centr. 1899, **70**, II, 800; 1900, **71**, I, 79; Chem. Ztg. 1899, **23**, 773, 1030; Jahr. Chem. 1899, **52**, 471; Wag. Jahr. 1899, **45**, 409; Zts. ang. Chem. 1899, **12**, 907, 1063.

2. Zts. Schiess. Spreng. 1906, **1**, 325.

3. Zts. Schiess. Spreng. 1906, **1**, 373.

is effected by the nitric acid itself,* and there is but little weak acid results, for the weak acid as fast as it is formed in the process, at once goes back into it. The apparatus comprizes the retort *A*, reaction column *B*, two columns *C*, *C* similar to *B*, and cooling worm *E*. Where a charge of 1500 kilos of niter is used the retort is 11.7 ft. long by 5.5 ft. in width, and weighs about 7 tons. One of the ends is closed at the bottom by a cast iron block luted with a sal ammoniac and iron filings cement, the end being provided with a discharging hole for the bisulfate.

The nitric acid vapors generated in *A*, rise through *B* and the worm *E*, which is cooled by flowing water from the outside. The acid condensing flows back into *B*, while the hot vapors meeting it here carry away all nitrogen oxides and chlorine. When flowing out of *B*, passes through a lead pipe slightly inclined towards the tower, and thus always remaining luted with acid, to prevent the escape of vapors. The pipe is in the lead box *F*, which receives the water from the coil *E*, and the acid from here runs into the receiver *D*. The acid vapors not condensed in *E*, are retained in the towers *C*, *C*. The first one is fed with 94% sulfuric acid, and as it flows out is pumped back into the second tower *C*. Only a slight feed of such acid is required to keep back the nitrogen oxide vapors, and this acid runs out of the bottom, about 200 k. per charge of about 25% HNO_3 , inclusive of 8%-10% N_2O_3 .

O. Guttman¹ has submitted figures indicating that the results of the Skoglund process are inferior to that obtained with his own apparatus. In the Guttman condensing system² as shown in Fig. 67, the principle is illustrated of building the condenser entirely of perpendicular pipes so adjusted that the fumes travel upwards and downwards, the acid being run off at the bottom into a common reservoir by means of hydraulically sealed branch pipes. These pipes are 8 ft. long with walls but $\frac{1}{2}$ inch thick. The gases enter the first of the pipes at *E*, alternately ascending and descending to the issue at *F*, depositing on their way the condensed liquid which trickles down to the receptacle *D*. The condensing pipes are connected by arranging their upper bends so as to alternately connect pipes of one row with those of the other. As the employment in this manner of long condensing

1. Zts. Schiess. Spreng. 1906, **1**, 376.

2. E. P. 8915, 1890; 14774, 1896. J. Dovell, E. P. 18137, 1896.

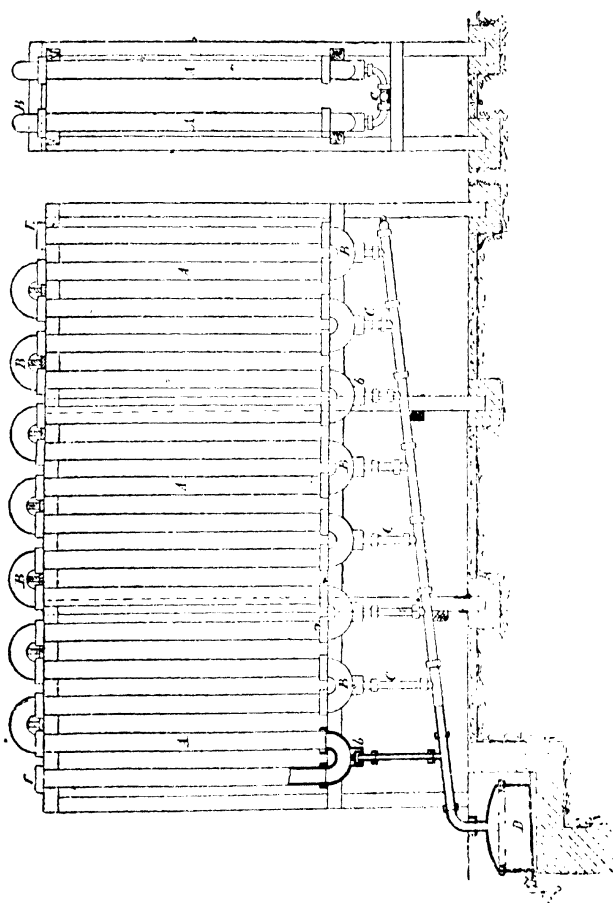


FIG. 67.—THE GUTTMAN NITRIC ACID CONDENSING SYSTEM

pipes presents an extended surface for condensation, it is evident that distillation may be carried on rapidly, the space normally occupied with numerous receiving vessels being thereby dispensed with. He has improved his system in many ways, as by the use of a compressed air injector immediately behind the exit tube of the still, where all of the uncondensed vapors are;¹ cooling with water instead of air;² arranging for condensing nitric acid at a comparatively high temperature, thus decreasing the liability of absorbing gases.³

W. Bate and F. Orme⁴ have improved the Guttman apparatus in the following particulars: (a) To insure more uniform circulation of the condensing water; (b) to enable a broken pipe to be replaced without interfering with the process; (c) and to avoid reducing the strength of the acid when a pipe cracks or leaks while the charge is being worked.⁵ An important point in connection with this system is the treatment of the vapors from the still with an air blast to oxidize the lower nitrogen oxides.⁶

In the method of E. Du Pont de Nemours Co.⁷ concentrated nitric acid is produced from mixtures of nitric and sulfuric acids, such as the waste acids obtained in the nitration of cellulose, containing 3%–25% HNO_3 by volume, and not less than 64% H_2SO_4 , by distributing the acid mixture uniformly over pieces of

1. O. Guttman, D. R. P. 73421, 160709; abst. Ber. 1892, **27**, 429; Chem. Centr. 1905, **76**, II, 89; Chem. Ztg. 1905, **29**, 1713; Chem. Zts. 1902, **1**, 14; 1906, **5**, 59; Wag. Jahr. 1894, **40**, 493.

2. O. Guttman, E. P. 18189, 1897.

3. O. Guttman, E. P. 13694, 1901; abst. J. S. C. I. 1901, **20**, 987.

4. E. P. 25790, 1902; abst. J. S. C. I. 1903, **22**, 212.

5. Badische Anilin u. Soda Fabrik, D. R. P. 233729; abst. J. S. C. I. 1911, **30**, 747; Chem. Zentr. 1911, **82**, 1388; Chem. Ztg. Rep. 1911, **35**, 271; Wag. Jahr. 1911, **57**, I, 466; Zts. ang. Chem. 1911, **24**, 949; Zts. Schiess. Spreng. 1911, **6**, 232. See also Guttman, Chem. Trade J. 1915, **56**, 311.

6. O. Guttman, U. S. P. 491481, 1893; 771629, 1904; abst. Chem. Zts. 1904, **3**, 811. See also W. Round, E. P. 9182, 1903; abst. J. S. C. I. 1904, **23**, 370. The J. Walter and C. Lehmann nitric acid generator is described in E. P. 20290, 1896; abst. Mon. Sci. 1898, **52**, 176. O. Guttman and L. Rohrmann, E. P. 22481, 1891. For the Borchers acid-resisting composition containing Cr, Mo and W oxides, see Belg. P. 259296, 1913. See Brante & Co., Swiss P. 8518, 1894. E. Brauer, Belg. P. 226490, 1910. J. Boot, Belg. P. 135160, 1898. F. Nathan, J. and W. Thomson, Belg. P. 218933, 1909. Norsk. Hydro-Elektrisk Kvälstofaktieselskab, Port. P. 8466, 8467, 8468, 8540; abst. Chem. Ztg. 1913, **37**, 44, 802. Norw. P. 22894; abst. Chem. Ztg. 1913, **37**, 241. U. S. P. 1324255, 1919; abst. J. S. C. I. 1920, **39**, 108-A. F. Raschig, Belg. P. 257558, 1913.

7. E. P. 135535, 1920. C. Rossi, Ital. P. 382/59, 124140; abst. Chem. Ztg. 1913, **37**, 200.

quartz or other suitable material, of 2"-3" diameter, in a tower at the lower end of which steam or a hot gas is admitted, the temperature of the vapors leaving the upper end of the tower being kept below 215° F., and preferably below 205° F. The vapors are passed to a condenser, and the uncondensed gases absorbed in water and returned to the tower. The distributor for the acids entering the tower is formed with liquid-discharging openings, and with openings through which vapors from the tower pass a coupling leading to the condenser.

The Deutsche Gasglühlicht A. G.¹ have described a process for the manufacture of highly concentrated nitric acid by the concentration of acid of not less than 69% strength, by distillation with approximately 78% sulfuric acid. The partially concentrated acid is then distilled in an apparatus fitted with a fractionating column to produce an acid of high concentration. Complete separation of the dilute nitric acid from the mixed acids remaining in the still is effected in a separate apparatus, and both the dilute nitric acid thus obtained and the sulfuric acid, after concentration to about 78% strength, are returned to the vessel in which the first concentration takes place.

F. Bayer has found² that if steam and air are passed through a mixture of nitric and sulfuric acids containing nitrous gases, and the resulting nitrous vapors are dried by means of sulfuric acid, the yield of 95%-96% nitric acid is almost quantitative. Any gases which pass out of the condenser are absorbed in sulfuric acid in a tower, and this acid then passes to the drying tower. Instead of pure sulfuric acid a mixture of sulfuric and nitric acids may be used as the drying agent. The amount of air and the dimensions of the condensing and drying apparatus depend on the amount of nitrous gases in the acid mixture. If there is much nitrous gas an oxidation chamber should be placed between the dryer and condenser. Also that when a mixture³ of concentrated sulfuric acid and dilute nitric acid flows down a tower packed with acid-resisting material, such as glass, quartz, or the like, and passes into an externally heated still or retort. An outlet siphon tube

1. D. R. P. 299681, 1916; abst. J. S. C. I. 1920, **39**, 62-A. H. Pauling, D. R. P. 257809, abst. Chem. Ztg. 1913, **37**, 262.

2. D. R. P. 297903, 1915; abst. J. S. C. I. 1920, **39**, 20-A. E. Collett, F. P. 450448; abst. Chem. Ztg. 1913, **37**, 244. New Zeal. P. 34032, 1914.

3. D. R. P. 297901, 1916; abst. J. S. C. I. 1920, **39**, 62-A.

is attached to the retort at a suitable height, e. g., half way up the side. The mixture of acids is so adjusted that nitric acid of the required strength distils over, and about 70% sulfuric acid flows out of the retort.

In the F. Gros and Bouchardy process,¹ strong nitric acid is obtained by passing into aqueous nitric acid, nascent nitric anhydride obtained by the reaction of ozone on NO_2 .

Condensing Nitric Acid by Means of Plate Towers.² The "plate towers" of G. Lunge and L. Rohrmann are much preferable to the coke towers for acid condensing purposes, in that coke has a decided reducing effect upon nitric acid forming nitrous acid and the lower nitrogen oxides. These plate towers are made of acid-resisting stoneware, and are so constructed as to present a large surface for purposes of condensation, while at the same time offer most intimate contact between the gases and liquids. These towers may advantageously be worked in conjunction with other cooling systems, acid worms, refrigerating receivers, and as supplementary and auxiliary to existing cooling arrangements where the capacity of the plant is to be increased from a production standpoint. They are explained more in detail in connection with the condensation of sulfuric acid vapors in the next chapter.

Continuous Nitric Acid Manufacture with Chili Saltpeter. The process of the Badische Anilin und Soda Fabrik³ involves passing the niter and vitriol through a series of stills heated independently to various temperatures, the contents being kept in mechanical motion. The temperatures maintained in the several chambers are 110° – 120° , 150° – 170° , 220° – 250° , 260° – 280° and 280° – 300° . The first chamber yields about 60% of the entire product as 96%–97% HNO_3 , the second chamber an acid of 88%–90%, the third chamber about 60% strength acid, the

1. E. P. 131335, 131336, 1918; abst. C. A. 1920, **14**, 103. M. Moest, R. Müller, von Berneck, J. Opl and Farbwerke Meister, Lucius & Brüning, U. S. P. 1050160; abst. Chem. Ztg. 1913, **37**, 244.

2. E. P. 29746, 1897; abst. J. S. C. I. 1897, **16**, 537.

3. D. R. P. 227377, 1908; abst. C. A. 1911, **4**, 1666; Mon. Sci. 1914, **81**, 85; Chem. Zentr. 1910, **81**, II, 1419; Chem. Ztg. Rep. 1910, **34**, 561; Chem. Zts. 1911, **10**, 2363; Jahr. Chem. 1910, **63**, I, 586; Wag. Jahr. 1910, **56**, I, 482; Zts. ang. Chem. 1910, **23**, 2338; Zts. Schiess. Spreng. 1910, **5**, 441; 1912, **7**, 36. F. P. 406969, 1909; abst. C. A. 1911, **4**, 1666; Mon. Sci. 1910, **73**, 175; Chem. Ztg. Rep. 1910, **34**, 126.

fourth chamber acid of about 15%, and the fifth chamber acid of 2%–5% strength only. From the last chamber flows a commercial bisulfate free from nitrogen. According to the H. Schellhass patent,¹ the vitriol and niter, heated and finely divided, are separately fed into the reaction chamber in such a manner that an intimate mixture of the two finely divided masses is effected, the sodium or potassium nitrate being first fused and then introduced through an atomizing nozzle with the aid of hot air. The acid is similarly introduced.

M. Prentice² causes the nitrate and sulfuric acid to flow through a distilling vessel from a charging opening to a siphon outlet for the residue, the acid gases passing off through suitable outlets. The distilling vessel may be divided into separate compartments.³ The F. Raschig⁴ continuous process for nitric acid manufacture, mixes NaNO_3 and H_2SO_4 and distills at about 170° under a high vacuum, continuously drawing off the nitric acid through a condenser and replenishing the mixture in the still by suction through a pipe, the end of which is submerged in a supply vessel and the height of which is adjusted to carry a head of liquid nearly corresponding to the vacuum in the still, then continuously drawing off the NaHSO_4 formed from the still through a pipe suitably adjusted as to height.

In another continuous process,⁵ niter and vitriol are simultaneously fed into a large bulk of molten bisulfate in a retort, the bisulfate being periodically withdrawn from the bottom of the

1. D. R. P. 241711, 1911; abst. C. A. 1912, **6**, 2152; Chem. Zentr. 1912, **83**, I, 172; Chem. Ztg. Rep. 1912, **36**, 8; Wag. Jahr. 1911, **57**, I, 469; Zts. ang. Chem. 1912, **25**, 136; Zts. Schiess. Spreng. 1912, **7**, 78.

2. E. P. 6960, 8902, 1893; abst. Mon. Sci. 1895, **46**, 50. D. R. P. 79045; abst. Ber. 1895, **28**, 482; Jahr. Chem. 1895, **48**, 569; Wag. Jahr. 1895, **41**, 450; Zts. ang. Chem. 1895, **8**, 170.

3. U. S. P. 526116, 1894. See Tentelew Chemical Works, E. P. Appl. 16671, 1916; J. S. C. I. 1916, **35**, 74.

4. U. S. P. 1130104, 1915; abst. C. A. 1915, **9**, 1099; J. S. C. I. 1915, **34**, 423. D. R. P. 283212, 1914; abst. C. A. 1915, **9**, 2576; Chem. Zentr. 1915, **86**, I, 925; Chem. Ztg. Rep. 1915, **39**, 165; Zts. ang. Chem. 1915, **28**, 248.

5. A. Klages and Saccharinfabrik Akt. Ges. vorm. Fahlberg, List & Co., U. S. P. 1099452, 1914; abst. C. A. 1914, **8**, 3103; Mon. Sci. 1914, **81**, 138. E. P. 3264, 1913. D. R. P. 267869; abst. C. A. 1914, **8**, 998; Chem. Zentr. 1914, **85**, I, 197; Chem. Ztg. Rep. 1913, **37**, 695; Wag. Jahr. 1913, **59**, I, 435; Zts. ang. Chem. 1914, **27**, 49. E. P. 464561, 1913; abst. Mon. Sci. 1916, **83**, 11; Chem. Ztg. Rep. 1914, **38**, 479. Aust. P. 66307. Belg. P. 260299, 1913. See also W. Garroway, E. P. 6777, 1899; abst. J. S. C. I. 1900, **19**, 349. Chemische Fabrik Rhénania, Belg. P. 154123, 155007, 1901. Swiss P. 24001, 1901.

retort by means of an overflow device, and in a fluid condition.

• **Fixation of Atmospheric Nitrogen.**¹ In 1898 W. Crookes

1. A. Badin, U. S. P. 1196639, 1916; abst. J. S. C. I. 1916, **35**, 1016; Mon. Sci. 1917, **84**, 10. E. P. 22586, 1914; abst. J. S. C. I. 1915, **34**, 353; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 119; Mon. Sci. 1917, **84**, 74. Can. P. 174685, 1917; abst. C. A. 1918, **12**, 208. H. Lee, L. Walker, H. Dutcher and E. Haggren, Mining Eng. Record, 1918, **23**, 73; abst. C. A. 1918, **12**, 1856. J. Bucher, J. Ind. Eng. Chem. 1917, **9**, 233. F. Lindquist, U. S. P. 1298363; abst. C. A. 1919, **13**, 1751. Badische Anilin & Soda Fabrik, D. R. P. 233729, 1910; abst. C. A. 1911, **5**, 2710; J. S. C. I. 1911, **30**, 747; Chem. Zentr. 1911, **82**, I, 1388; Chem. Ztg. Rep. 1911, **35**, 271; Wag. Jahr. 1911, **57**, I, 466; Zts. ang. Chem. 1911, **24**, 949; Zts. Schiess. Spreng. 1911, **6**, 232. Beilby, E. P. Appl. 21373, 1919; abst. J. S. C. I. 1919, **38**, 700-A. G. McCourt and C. Ellis, U. S. P. 1280496; abst. C. A. 1919, **13**, 774. W. Landis, U. S. P. 1103060, 1103061, 1103062; abst. J. S. C. I. 1914, **33**, 864; C. A. 1914, **8**, 2981; Mon. Sci. 1914, **81**, 178. U. S. P. 1149653, 1154640, 1163095, 1183885, 1193796, 1193797, 1193798, 1193799, 1193800; abst. J. S. C. I. 1915, **34**, 489, 961, 1207; 1916, **35**, 115, 737, 963; Chem. Ztg. Rep. 1916, **40**, 429; 1917, **41**, 124, 167; J. Ind. Eng. Chem. 1915, **7**, 433; Met. Chem. Eng. 1915, **13**, 218; 1916, **14**, 260; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 120; 1917, **2**, 187; Mon. Sci. 1916, **83**, 35, 37, 49; 1917, **84**, 5, 10. J. Montgomery, Chem. Eng. 1918, **27**, 35; C. A. 1919, **13**, 996; J. Ind. Eng. Chem. 1919, **11**, 391. Brightmore, E. P. Appl. 21318, 1918; abst. J. S. C. I. 1919, **38**, 31-A. R. Pearson and H. Parkes, E. P. 130693; J. S. C. I. 1919, **38**, 718-A. R. Pearson, New Zeal. P. 41421, 1919. Y. Morimoto, J. Chem. Ind. Tokyo, 1918, **21**, 881; J. S. C. I. 1919, **38**, 10-A. H. Barschall, D. R. P. 259877, 1911; abst. C. A. 1913, **7**, 3205; Chem. Zentr. 1913, **84**, II, 107; Chem. Ztg. Rep. 1913, **37**, 320; Wag. Jahr. 1913, **59**, I, 535; Zts. ang. Chem. 1913, **26**, 382. Buch, J. Gasbeleuch. 1919, **62**, 2; abst. J. S. C. I. 1919, **38**, 219-A. Bureau d'Organisation Economique, Rev. de l'ingenieur et index Technique, 1919, **25**, 15; abst. C. A. 1919, **13**, 3286. H. Creighton, J. Frank. Inst. 1919, **187**, 377; abst. C. A. 1919, **13**, 1130. Lefebvre, E. P. 1045, 1859; abst. Mon. Sci. 1906, **65**, 336. H. Fulmer, Soil Sci. 1917, **4**, 1; abst. J. S. C. I. 1917, **36**, 1021. Sprengluft Ges., D. R. P. 312286; J. S. C. I. 1919, **38**, 681-A. A. Sanfourche, Compt. rend. 1919, **168**, 307; C. A. 1919, **13**, 1192. Bull. Soc. Chim. 1919, **25**, 633; abst. J. S. C. I. 1920, **39**, 154-A. Elektrizitätswerk Lonza, Norw. P. 28062, 1918; abst. C. A. 1919, **13**, 502. Swiss P. 73574, 1916. A. Stähler and J. Elbert, Ber. 1913, **46**, 2060; J. S. C. I. 1913, **32**, 789. M. Guichard, Rev. Sci. 1918, **56**, 385; abst. C. A. 1918, **12**, 1941. F. Howles, J. S. C. I. 1907, **26**, 298, 452. M. Berthelot, Compt. rend. 1906, **142**, 1367; abst. C. A. 1907, **1**, 22. C. Steinmetz, C. A. 1918, **12**, 2494. N. Kameyama, J. Chem. Ind. (Japan), 1919, **22**, 469; abst. C. A. 1919, **13**, 2738. Nitrogen Products Co., E. P. Appl. 15765, 1919; abst. J. S. C. I. 1919, **38**, 484-A. R. Strutt, Proc. Roy. Soc. 1911, **85-A**, 533; J. S. C. I. 1911, **30**, 1261. A. Foss, U. S. P. 1175252; abst. J. S. C. I. 1916, **35**, 548. H. Prinsen-Gerlign, De Suikerindustrie, 1917, 279, 311; Arch. Suikerind. 1918, **26**, 532; abst. C. A. 1919, **13**, 903. Schiller, Apoth. Ztg. 1919, **34**, 167; abst. C. A. 1919, **13**, 3286. C. Limp, E. P. 403536; abst. Mon. Sci. 1911, **75**, 571, 573. C. Williams, Elec. World, 1919, **73**, 281, 443; abst. C. A. 1919, **13**, 537, 1282. M. Tausent, Zts. Elektrochem. 1912, **18**, 314; J. S. C. I. 1912, **31**, 498. C. Luckow, D. R. P. 179305; abst. Chem. Zentr. 1907, **78**, I, 1163; Chem. Ztg. Rep. 1907, **30**, 31; Jahr. Chem. 1905-1908, I, 3060; Wag. Jahr. 1906, **52**, I, 510; Zts. ang. Chem. 1907, **20**, 1748. G. Taylor, J. Capps, A. Coolidge, J. Ind. Eng. Chem. 1918, **10**, 270; J. S. C. I. 1918, **37**, 298-A. P. Bunet, U. S. P. 1196657, 1916; abst. J. S. C. I. 1916, **35**, 1016; Mon. Sci. 1917, **84**, 10. E. P. 4287, 1915; abst. J. S. C. I. 1915, **34**, 961; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 119; Mon. Sci. 1917, **84**, 76.

forcibly pointed out that the commercial fixation of nitrogen was one of the great problems awaiting the reflection and ingenuity of chemists, and that the economic independence of a nation in peace and in war, was primarily dependent upon the proper solution of this problem, and convincingly emphasized with

R. McKee, Can. P. 188363, 1919; abst. C. A. 1919, **13**, 502. S. Sachs, Ann. Physik. 1915, (4), **47**, 886; abst. J. S. C. I. 1915, **34**, 1257. S. Tucker and H. Read, Met. Chem. Eng. 1912, **10**, 745; J. S. C. I. 1912, **31**, 1124. C. Volney, Trans. Amer. Electrochem. Soc. 1903, **3**, 285; J. S. C. I. 1903, **22**, 954. G. Erlwein, Electrochem. Ztg. 1906, **13**, 137, 161. R. Wallace and E. Wassmer, New Zeal. P. 32242, 1913. G. Wiegner, J. Landw. 1913, **61**, 11; Kolloid Zts. 1914, **14**, 55; J. S. C. I. 1914, **33**, 1164. R. Williams, U. S. P. 1314231; C. A. 1919, **13**, 2747. T. Ewan and J. Napier, J. S. C. I. 1913, **32**, 467. Chem. Fabr. Gladbeck, G. m. b. h., F. P. 6484, 1906, addn. to F. P. 341109; abst. Mon. Sci. 1906, **65**, 4; 1909, **71**, 571. O. Döbelstein, Stahl. u. Eisen, **32**, 1571; abst. C. A. 1913, **7**, 219. E. Haslup, Can. P. 187050, 1918; abst. C. A. 1918, **12**, 2670. N. Tommasi, Can. P. 185847, 1918; abst. C. A. 1918, **12**, 2045. J. Bucher, U. S. P. 1174667, 1174668, 1916; abst. J. S. C. I. 1916, **35**, 468; Mon. Sci. 1917, **84**, 13. U. S. P. 1113598, 1113599, 1914; abst. J. S. C. I. 1914, **33**, 1154; C. A. 1914, **8**, 3762; Mon. Sci. 1915, **82**, 17. U. S. P. 1174944; abst. J. S. C. I. 1916, **35**, 469. J. Currie, U. S. P. 1263533, 1918; abst. J. S. C. I. 1918, **37**, 335-A. E. P. 105953, 1916; abst. J. S. C. I. 1917, **36**, 656; 1918, **37**, 335-A. F. Fieschi, L'Industrie chim. 1918, **5**, 79; abst. C. A. 1918, **11**, 1478. A. Foss, Can. P. 175887, 1917; abst. C. A. 1917, **11**, 3101. DuPont Powder Co., E. P. 17038, 1912; abst. C. A. 1914, **8**, 302; J. S. C. I. 1913, **32**, 487. F. P. 446269; abst. J. S. C. I. 1913, **32**, 141. C. Senes and L. Ginies, F. P. 414726; abst. J. S. C. I. 1910, **29**, 1212; Mon. Sci. 1911, **75**, 572. Societe Anonyme le Nitrogene, Swiss P. 44750, 44751, 1908. I. Cederberg, Can. P. 185119, 1918; abst. C. A. 1918, **12**, 1818. F. Hausser, E. P. 7419, 1914; abst. C. A. 1915, **9**, 2435; J. S. C. I. 1915, **34**, 800. F. P. 469649, 1914; abst. J. S. C. I. 1915, **34**, 80. A. Gorboff and B. Mitkevitch, D. R. P. 190614, 1906; abst. J. S. C. I. 1908, **27**, 576; Chem. Ztg. Rep. 1907, **31**, 635; Wag. Jahr. 1907, **53**, II, 212. A. Cocking and Kynoch, Ltd., E. P. 123444; abst. J. S. C. I. 1919, **38**, 360-A. W. Siebert, U. S. P. 1061786; abst. J. S. C. I. 1913, **32**, 665; C. A. 1913, **7**, 2163. E. Briner, J. Chim. Phys. 1915, **13**, 18; abst. J. S. C. I. 1915, **34**, 550. E. Briner and P. Naville, Helvet. Chim. Acta, 1919, **2**, 348; abst. Chim. Ind. 1920, **3**, 211. E. Briner and Baerfus, Helvet. Chim. Acta, 1919, **2**, 95. A. Neuberger, U. S. P. 850392, 1904; abst. Chem. Ztg. Rep. 1907, **31**, 255. W. Cramp and B. Hoyle, abst. J. S. C. I. 1909, **28**, 95. W. Werner, U. S. P. 777987 to 777991; J. S. C. I. 1905, **24**, 95; Mon. Sci. 1906, **65**, 336. Elektrizitätswerk Lonza, D. R. P. 302671, 1916; abst. J. S. C. I. 1918, **37**, 335-A; Mon. Sci. 1918, **85**, 60; Chem. Zentr. 1918, **89**, I, 319; Chem. Ztg. Rep. 1918, **42**, 44. Electrochem. Met. Ind. **5**, 485, 491; abst. C. A. 1908, **2**, 573. H. Pauling, E. P. 22322, 1910; abst. J. S. C. I. 1911, **30**, 84. O. Schönherr and J. Hessberger, U. S. P. 1115249, 1914; abst. J. S. C. I. 1914, **33**, 1162. R. Pictet, F. P. 409787, 1909; abst. J. S. C. I. 1910, **29**, 817. P. Guye, F. P. 441022, 1910; abst. J. S. C. I. 1911, **30**, 541. S. de Ferranti, E. P. 20697, 1907; abst. J. S. C. I. 1908, **27**, 1058. E. P. 13965, 1906; abst. J. S. C. I. 1907, **26**, 1145; Chem. Ztg. Rep. 1907, **31**, 562. U. S. P. 898346; abst. J. S. C. I. 1907, **26**, 1145; Zts. ang. Chem. 1908, 554. A. Grau and F. Russ, Sitzungsber. Akad. Wiss., Wien, 1906, **115**, II, A, 1; **117**, II, A, 321; J. S. C. I. 1907, **26**, 619; 1908, **27**, 945; Chem. Zentr. 1908, **79**, II, 667. W. Kochmann, U. S. P. 1055331; abst. J. S. C. I. 1913, **32**, 425; Arbeit. Pharm. Inst. Berlin, **8**, 81; Chem. Zentr. 1912, **83**, I, 169; C. A. 1912, **6**, 2295; 1913, **7**, 1445. E.

tangible figures what an important practical bearing this problem exerted on the future welfare and perpetuity of the civilized world.

He, with other scientists, brought forcibly to the attention of engineers and chemists the fact that the existing sources of available nitrogen were limited, and materially stimulated the

- Haslup, U. S. P. 1310478; abst. C. A. 1919, **13**, 2427. E. P. Appl. 17365, 1917; abst. J. S. C. I. 1918, **37**, 675-A. J. Island, U. S. P. 1316445, 1317705; abst. C. A. 1919, **13**, 2817, 3289; J. S. C. I. 1919, **38**, 819-A. E. P. Appl. 21690, 1919; abst. J. S. C. I. 1919, **38**, 700-A. New Zeal. P. 33642, 1913. J. Island and B. Coleman, Can. P. 197827, 1920. D. Helbig, F. P. 385193, 1907; abst. J. S. C. I. 1908, **27**, 576; Mon. Sci. 1911, **75**, 571, 573; Chem. Ztg. Rep. 1908, **32**, 333. E. P. 27790, 1907; abst. J. S. C. I. 1908, **27**, 817. A. Kaufman, U. S. P. 1307362; abst. C. A. 1919, **13**, 2259. Badische Anilin & Soda Fabrik, F. P. 350620; abst. J. Soc. Dyers, 1905, **21**, 182; Mon. Sci. 1906, **65**, 101. U. S. P. 1029528, 1054901, 1102715, 1158167; abst. J. S. C. I. 1912, **31**, 642; 1913, **32**, 365; 1914, **33**, 831; 1915, **34**, 1209. E. P. 26749, 1910; 8462, 1914; abst. J. S. C. I. 1912, **31**, 385; 1915, **34**, 822. Swiss P. 50538, 51899, 1910. A. Koenig, Zts. Elektrochem. 1915, **21**, 267; abst. J. S. C. I. 1915, **34**, 1090. H. Runge, F. P. 469793, 1914; abst. J. S. C. I. 1915, **34**, 29. Akt. Kvalveindustrie, New Zeal. P. 42156, 1919. J. La Cour, U. S. P. 1290584; abst. C. A. 1919, **13**, 688. F. Long, Elec. Rev. West. Elec. 1917, **71**, 65; abst. C. A. 1917, **11**, 2304. D. Lovejoy, U. S. P. 829272, 829273, 829274, 829275, 829276, 829277, 1906; abst. C. A. 1907, **1**, 99; J. S. C. I. 1906, **25**, 936. For the production of O and N from the air, using calcium plumbate, see G. Kassner, D. R. P. 234849, 1910; abst. J. S. C. I. 1911, **30**, 895; Chem. Zentr. 1911, **82**, I, 1726; Chem. Ztg. Rep. 1911, **35**, 304; Wag. Jahr. 1911, **57**, I, 543; Zts. ang. Chem. 1911, **24**, 1194. S. Nauckhoff, Met. Chem. Ind. 1917, **17**, 525; abst. C. A. 1918, **12**, 406. H. Rankin, F. P. 479492, 1915; abst. J. S. C. I. 1916, **35**, 1108. See also U. S. P. 1150786, 1915; abst. J. S. C. I. 1915, **34**, 960; 1916, **35**, 1108; Mon. Sci. 1916, **83**, 35; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 185. A. Stahler and J. Elbert, Ber. 1913, **46**, 2060. S. Peacock, U. S. P. 1143132; abst. J. S. C. I. 1915, **34**, 834; Mon. Sci. 1916, **83**, 34. L. Glaser, U. S. P. 921975; abst. J. S. C. I. 1909, **28**, 656; Mon. Sci. 1909, **71**, 140; Chem. Ztg. Rep. 1909, **33**, 399. J. Rudolphs and G. Thissell, D. R. P. 253080, 1911; abst. C. A. 1913, **7**, 686; Chem. Zentr. 1912, **83**, II, 1853; Chem. Ztg. Rep. 1912, **36**, 652; Wag. Jahr. 1912, **58**, I, 496; Zts. ang. Chem. 1912, **25**, 2551. H. Moody and S. Tucker, U. S. P. 1175007, 1916; abst. J. S. C. I. 1916, **35**, 469; Mon. Sci. 1917, **84**, 11. H. Lamb, U. S. P. 1123763, 1915; abst. J. S. C. I. 1915, **34**, 228. C. Dövic, U. S. P. 1194606, 1204349; abst. J. S. C. I. 1916, **35**, 1023, 1267. O. Silberrad, E. P. Appl. 12107, 1913. G. Kettler, Aust. P. 41303. Swiss P. 40882, 1907. W. Hoofnagle, F. P. 448519; abst. J. S. C. I. 1913, **32**, 432. India P. 3805, 1918. Can. P. 189634, 1920. E. Edwin, U. S. P. 1193882; abst. J. S. C. I. 1916, **35**, 971. E. Kilburn Scott, Electrician, 1916, **78**, 215, abst. C. A. 1917, **12**, 315; Trans. Amer. Electrochem. **34**; Gen. Elec. Rev. 1918, **21**, 793; Chem. Met. Eng. 1918, **19**, 411. W. Hemingway, U. S. P. 781826, 1905; abst. Chem. Ztg. 1905, **29**, 223; Chem. Zts. 1905, **4**, 269. A. Helfenstein, E. P. 26371, 1911; abst. C. A. 1913, **7**, 1679; J. S. C. I. 1912, **31**, 1136; Chem. Ztg. Rep. 1913, **37**, 307. F. P. 436828; abst. J. S. C. I. 1912, **31**, 499. D. Helbig, U. S. P. 887326; abst. Mon. Sci. 1909, **71**, 124. F. P. 352090, 1905; abst. J. S. C. I. 1905, **24**, 896; Mon. Sci. 1906, **65**, 102; 1911, **75**, 572, 573. U. S. P. 926413; abst. Chem. Ztg. Rep. 1909, **33**, 427. F. P. 385193; abst. Mon. Sci. 1911, **75**, 571, 573; Chem. Ztg. Rep. 1908, **32**, 333. D. R. P. 189864; abst. J. S. C. I. 1908, **27**, 576; Zts. ang. Chem. 1905, **18**, 1762; 1908, **21**, 556; Chem. Centr. 1903, **74**, II, 210; 1907, **78**, II

efforts of investigators in this field. The problem, in a more or less crude manner, had engaged the attention of research for over a century, but its solution had been approached primarily from the chemical side, and it was not until the researches of J. Liebig and others¹ on the biological transformation of elemental nitro-

1953; Zts. Electrochem. 1906, **12**, 550; Chem. Ztg. Rep. 1907, **31**, 585; Chem. Zts. 1907, **6**, No. 434; Jahr. Chem. 1905-1908, I, 1769; Wag. Jahr. 1907, **53**, I, 397. J. Ephraim, D. R. P. 276718; abst. J. S. C. I. 1914, **33**, 1154; Chem. Zentr. 1914, **85**, II, 550; Chem. Ztg. Rep. 1914, **38**, 465; Wag. Jahr. 1914, **60**, I, 438; Zts. ang. Chem. 1914, **27**, 536. Anon. Chem. Trade J. 1908, **43**, 441; abst. C. A. 1909, **2**, 360. Engrais, **25**, 212; abst. C. A. 1911, **5**, 1168. J. Ind. Eng. Chem. 1916, **8**, 1088; abst. C. A. 1917, **11**, 270. Iron Age, 1916, **97**, 1156; abst. C. A. 1916, **10**, 1777. J. S. C. I. 1915, **34**, 113; abst. Ann. Rept. Soc. Chem. Ind. 1916, **1**, 115. J. S. C. I. 1917, **36**, 1196. Met. Chem. Eng. 1918, **18**, 77. Nature, 1917, **100**, 316. Electrician, 1917, **80**, 131. Chem. News, 1917, **166**, 240. C. A. 1918, **12**, 295, 604. K. Den. Jap. P. 32722, 1918; abst. C. A. 1918, **12**, 2168. A. Koch, Centr. Bakt. Par. 1910, ii, **27**, 1; J. C. S. 1910, **98**, ii, 536; fixes nitrogen in the soil with the help of cellulose as source of energy. H. Pringsheim, Centr. Bakt. Par. 1910, **26**, II, 222; abst. J. C. S. 1910, **98**, ii, 230. E. Scott, Belg. P. 257874, 1913. J. Bucher, Belg. P. 252581, 1913; abst. Chem. Ztg. 1913, **37**, 802. Chemische Fabrik Gladbeck Ges., Belg. P. 176100, 1904. Comité d'initiative pour la lab. de produits nitrique, Belg. P. 172521, 1903. Chemische Fabrik Buckau, Belg. P. 195551, 1906. Compare also F. P. 335453, 341109, 353548, 358171, 363617, 363618, 365070, 369387, addn. 6184 to 341109, 371397, 375349, 379437, 380467, 380614, 380884, 385193, 391693, 391557, 402012, 405493, 411693, 415976, 416557, 419782, addn. 12414, 12656, to 402012, addn. 12415 to 406115, 431182, 435397, 440217, 440218, 441706, addn. 15525 to 440217.

1. J. v. Braun, Abegg's Handb. d. anorg. Chem. 1907, **3**, III, 216. A. Stewart, Recent Advances in Physical and Inorganic Chemistry, 1909, 39. A. Crossley, Pharm. J. 1910, (4), **30**, 329; abst. C. A. 1910, **4**, 1270. A. Peterson, U. S. P. 880037, 880464, 1904; abst. Chem. Ztg. Rep. 1908, **32**, 252. F. P. 349227, 1904. D. R. P. 185897, 1904; abst. J. S. C. I. 1902, **21**, 557; 1905, **24**, 679; Mon. Sci. 1909, **71**, 160; Chem. Zentr. 1907, **78**, II, 650; Chem. Ztg. Rep. 1907, **31**, 343; Jahr. Chem. 1905-1908, I, 1767; Wag. Jahr. 1907, **53**, I, 394; Zts. ang. Chem. 1908, **21**, 557. R. Pawlikowski, E. P. 26728, 1905; abst. J. S. C. I. 1906, **25**, 638. J. Mitchell and D. Parks, U. S. P. 817082, 1906. L. Summers, U. S. P. 1125208; abst. J. S. C. I. 1915, **34**, 236; Proc. Amer. Inst. Elec. Eng. 1915, **34**, 337; Met. Chem. Eng. 1915, **12**, 241; Trans. Amer. Elec. Soc. 1915, **27**, 339. O. and K. Weber, U. S. P. 1042179; abst. C. A. 1912, **6**, 3370. F. P. 436201; abst. J. S. C. I. 1912, **33**, 432. F. Russ, Oest. Chem. Ztg. 1907, **10**, 237; Zts. ang. Chem. 1907, **21**, 555; Zts. Electrochem. 1913, **19**, 923. G. Wagener, U. S. P. 1055003, 1055295; abst. J. S. C. I. 1913, **32**, 432; C. A. 1913, **7**, 1331. E. Salvador, Gazz. chim. ital. 1900, **30**, II, 389; Chem. Ztg. 1901, **25**, 9; J. C. S. 1900, **80**, ii, 94. J. Thoresen and F. Tharaldsen, E. P. 13689, 1905; abst. J. S. C. I. 1906, **25**, 321. F. P. 352556; abst. J. S. C. I. 1905, **24**, 976. O. Kausch, Electrochem. Zts. 1906, **13**, 63. E. Scott, U. S. P. 1113376; abst. C. A. 1914, **8**, 3762; Mon. Sci. 1915, **82**, 30. E. P. 14871, 16014, 1912; abst. J. S. C. I. 1913, **32**, 872; C. A. 1914, **8**, 22, 23; Chem. Ztg. Rep. 1913, **37**, 657. E. P. 4723, 4725, 6136, 1913; abst. J. S. C. I. 1914, **33**, 361, 427; Chem. Ztg. Rep. 1915, **39**, 20; C. A. 1914, **8**, 2654, 2849. F. P. 459660. New Zeal. P. 33472, 1913. E. Scott and G. Hager, E. P. 866, 1913; abst. J. S. C. I. 1913, **32**, 664; C. A. 1914, **8**, 2121; Chem. Ztg. Rep. 1914, **38**, 376. E. Scott and F.

gen into available and assimilable forms, and the interdependence of electro-thermal considerations upon the influence of the combination of atmospheric nitrogen and oxygen, that the problem emerged from the chaotic to the tangible phase.

The earlier efforts in the art were largely confined to the commercial attempts of nitrogen fixation for the purpose of manufacturing cyanides and nitrides, and the earlier bibliography of the subject, therefore, is mainly concerned with efforts in this direction.

The three fundamental economic products formed by the union of atmospheric nitrogen are: (a) its union with oxygen to form nitrites or nitrates; (b) coupling with carbon to form cyanides (XCN), and cyanamides (XCN₂); and (c) combination with hydrogen to form ammonia (NH₃). From all the above products a large number of derivatives are obtainable of paramount value in the chemical arts. The most important of these commercial products are the unions with oxygen, with the subsequent formation of nitric acid and the nitrates of commerce.

It has been only within the last half-decade that the full significance of the previous observations have been so correlated as to be fully recognized, and the biological cycle of transformations which nitrogen underwent in nature in which physiological processes play so leading a part, revealed nitric acid and its derivatives as not merely useful chemical reagents, but as indis-

- Howles, E. P. 3953, 1915; abst. J. S. C. I. 1916, **35**, 476. E. P. 126058, 126080; abst. J. S. C. I. 1919, **38**, 346-A, 469-A. India P. 3221, 1917. E. Scott, J. S. C. I. 1915, **34**, 113, 258; J. Roy. Soc. Arts, 1912, **60**, No. 3104, 645; Smithsonian Report, 1913, 359 Publication 2291. Iron Age, 1916, **98**, 305; abst. J. S. C. I. 1916, **10**, 2503; J. S. C. I. 1915, **34**, 126; 1917, **36**, 771, 810, 915. J. de Kowalski, Compt. rend. 1914, **158**, 625; J. S. C. I. 1914, **33**, 311; Bull. Soc. Intern. Electriciens, 1903, **3**, 314; Éclairage Électrique, 1903, **37**, 505; Oest. Chem. Ztg. 1912, Nos. 17, 18. M. Kroczeck, Gas World, 1913, **59**, 378; abst. C. A. 1913, **7**, 3922. For the drying by refrigeration of air to be liquefied, G. Claude, Compt. rend. 1913, **157**, 466; abst. J. S. C. I. 1913, **32**, 943. H. Colin and E. Geisenberger, Belg. P. 144429, 1899. G. Kassner, Swiss P. 57767, 1911. C. Casman, Belg. P. 256596, 1913. Anon., Elec. World, **72**, 894; abst. C. A. 1919, **13**, 8. Anon., Chem. Met. Eng. 1919, **21**, 66; abst. C. A. 1919, **13**, 2109. Anon., Manufacture Rec. 1919, **75**, No. 25, 89; abst. C. A. 1919, **13**, 1903. See also C. A. 1919, **13**, 399, 1518. Anon., J. pour Électrique, 1919, **28**, 15; abst. C. A. 1919, **13**, 537. Anon., Chem. Trade J. 1919, **64**, 521; abst. C. A. 1919, **13**, 1891. J. S. C. I. 1919, **38**, 189-R. Anon., Chem. Met. Eng. 1919, **21**, 612; abst. C. A. 1920, **14**, 598. Anon., Elect. Rev. 1919, **75**, 1053; abst. C. A. 1920, **14**, 496. H. Andriessens, Zts. Elektrochem. 1919, **25**, 255; abst. C. A. 1920, **14**, 384. I. Cederberg and G. Kynceberger, Can. P. 185119, 1918. Soc. Generale des Natrures, Can. P. 174685, 1917, 164839, 1915.

pensable requisites and potent factors in the well-being of man. Inorganic nitrates are gone when the Chili saltpeter beds have become exhausted. Basic available nitrogen is substantially at an end when the supply of ammonia is diminished when the world's supply of coal is gone.

It is well recognized in the nitrogen problem, that ammonia and nitric acid stand in a clearly defined relation to each other, which is not affected by the consideration that sooner or later the world must face a diminution in the supply of combined (synonymous with available) nitrogen. This situation will--and recently has--changed materially by successful processes for the use of the inexhaustible supplies of nitrogen in the atmosphere, and in the international conflict so recently terminated, it has been said that Germany was enabled to prolong hostilities due in a great measure to the fact that she has been able to so perfect the commercial exploitation of nitrogen fixation in attempts to bind nitrogen and keep it securely bound either in derivatives of ammonia or of nitric acid, as to become entirely independent of Chili saltpeter or nitrogen as coal by-products.¹

It is from such conditions as these that have sprung the manifold successful processes for harnessing this chemically inert element, previous series of observations having now acquired a tangible significance. The economically developed methods for the fixation of nitrogen and its union with oxygen to oxides, afterwards oxidizable into nitric acid and then neutralizable into salts, are those developed by O. Schönherr and his co-workers; by K. Birkeland and S. Eyde in the utilization of the vast water power in Norway; and in the process as primarily developed by years of experimentation by Pauling. Each of these processes are detailed herein.

1. Anon., *Nature*, 1920, **104**, 533; *Elec. Rev.* 1920, **76**, 403; abst. C. A. 1920, **14**, 1187. A. Acker and Nitrogen Co., U. S. P. 1051303, 1913; abst. *Chem. Ztg.* 1913, **37**, 244. Akt. Ges. für Stickstoffdünger, D. R. P. Ann. A-22179; abst. *Chem. Ztg.* 1913, **37**, 215. American Nitro Products Co., Can. P. 161568, 1915. Armour Fertilizer Works, Can. P. 175750, 175751, 1917. Atmospheric Products Co., E. P. 14781, 1902; India P. Appl. 196, 1902, 158, 1903; E. P. 8236, 1901; 14781, 1902. O. Bender, D. R. P. 258935; abst. *Chem. Ztg.* 1913, **37**, 387. Canadian Explosives Ltd., Can. P. 179118, 1917; 142472, 1912. Meister, Lucius & Brüning, E. P. 3662, 1913; abst. *Chem. Ztg.* 1913, **37**, 348, 397. Belg. P. 253381; General Chemical Co., Can. P. 142481, 1912. C. Greenstreet, U. S. P. 1052815, 1913; abst. *Chem. Ztg.* 1913, **37**, 348. J. Hager and Lever Brothers, E. P. 131684, 1918; abst. C. A. 1920, **14**, 323. F. Hlavati, Belg. P. 252772; abst. *Chem. Ztg.* 1913, **37**,

Schönherr Process for Manufacturing Nitric Acid.¹ In 1905

O. Schönherr in conjunction with the engineer J. Hessberger, both

348. W. Iwanoff, Can. P. 181048, 1917. F. Johnson, Can. P. 187937, 1918. McCourt and Ellis, E. P. 25629, 1912; abst. Chem. Ztg. 1913, **37**, 254. Norsk. Hydro-Elektrisk Kvaestofaktieselskat, Can. P. 157489, 157490, 1914, 161131, 1915; 170816, 1916; 175887, 1917. R. Nowicki, Aust. P. Ann. 348, 1912; abst. Chem. Ztg. 1913, **37**, 316. R. Pictet, E. P. 19254, 1900; India P. Appl. 219, 1902. L. Simpson, Chem. Met. Eng. 1920, **22**, 20; abst. C. A. 1920, **14**, 1187. L'Air, Liquid Societe anonyme pour l'Etude et l'Exploitation des Procèdes Georges Claude, Can. P. 182010, 1918. Societe Generale des Nitrures, Span. P. 53970; abst. Chem. Ztg. 1913, **37**, 228. Southern Electro Chemical Co., Can. P. 153539, 1914. The Surface Combustion Inc., Can. P. 187662, 1918. V. Thrane, Can. P. 185670, 1918. Les Usines Electriques de la Lonza, Can. P. 185847, 1918. Wallace and Wassmer, E. P. 3147, 1912; New Zeal. P. 32242, 1912; E. P. 448511; abs. Chem. Ztg. 1913, **37**, 284; A. White, Chem. Met. Eng. 1920, **22**, 369; J. Ind. Eng. Chem. 1919, **11**, 231; abst. C. A. 1919, **13**, 772; 1920, **14**, 1187. E. Wiley, Can. P. 146912, 1913. J. Wood, Can. P. 160962, 1915.

I. D. R. P. Ann. B. 54700. D. R. P. 168601, abst. Chem. Centr. 1906, **77**, I, 1303; Chem. Ztg. 1906, **30**, 361; Jahr. Chem. 1905-1908, I, 1763; Wag. Jahr. 1905, **52**, I, 455; Zts. ang. Chem. 1906, **19**, 1522. D. R. P. 188188, abst. Mon. Sci. 1910, **73**, 65; Chem. Zentr. 1907, **78**, II, 1282; Chem. Ztg. Rep. 1907, **31**, 492; Chem. Zts. 1907, **6**, No. 200; Jahr. Chem. 1905-1908, I, 1779; Wag. Jahr. 1907, **53**, I, 413. D. R. P. 191912; abst. Mon. Sci. 1910, **73**, 67; Chem. Zentr. 1908, **79**, I, 315; Chem. Ztg. Rep. 1907, **31**, 633; Chem. Zts. 1908, **7**, 490; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1907, **53**, I, 410; Zts. ang. Chem. 1908, **21**, 798; Zts. Schiess. Spreng. 1907, **2**, 455. D. R. P. 196323; abst. J. S. C. I. 1908, **27**, 576; Mon. Sci. 1911, **75**, 58; Chem. Zentr. 1908, **79**, I, 1341; Chem. Ztg. Rep. 1908, **32**, 245; Jahr. Chem. 1905-1908, I, 1721; Wag. Jahr. 1908, **54**, I, 465; Zts. ang. Chem. 1908, **21**, 1521. D. R. P. 200986; abst. J. S. C. I. 1911, **30**, 1058; Mon. Sci. 1911, **75**, 82; Chem. Zentr. 1908, **80**, II, 838; Chem. Ztg. Rep. 1908, **32**, 489; Jahr. Chem. 1905-1908, I, 2058; Wag. Jahr. 1908, **54**, II, 24; Zts. ang. Chem. 1908, **21**, 2040. D. R. P. 201279; abst. Chem. Zentr. 1908, **79**, II, 1139; Chem. Ztg. Rep. 1908, **32**, 532; Chem. Zts. 1908, **7**, No. 1012; Jahr. Chem. 1905-1908, I, 1772; 1909, **62**, 529; Wag. Jahr. 1908, **54**, I, 410; Zts. ang. Chem. 1908, **21**, 2330. D. R. P. 204997, abst. Chem. Zentr. 1909, **81**, I, 112; Chem. Ztg. Rep. 1908, **32**, 683; Chem. Zts. 1909, **8**, No. 1297; Jahr. Chem. 1909, **62**, 529; Wag. Jahr. 1908, **54**, I, 411; Zts. ang. Chem. 1909, **22**, 168. D. R. P. 210167; abst. J. S. C. I. 1909, **28**, 656; Mon. Sci. 1912, **77**, 97; Chem. Zentr. 1909, **80**, I, 77; Chem. Ztg. Rep. 1909, **33**, 314; Jahr. Chem. 1909, **62**, 535; Wag. Jahr. 1909, **55**, I, 416; Zts. ang. Chem. 1909, **22**, 1318; Zts. Schiess. Spreng. 1909, **4**, 235. U. S. P. 1115164, 1914; abst. J. S. C. I. 1914, **33**, 1154; Mon. Sci. 1915, **82**, 18. D. R. P. 212051, abst. Chem. Zentr. 1909, **80**, II, 484; Chem. Ztg. Rep. 1909, **33**, 420; Wag. Jahr. 1909, **55**, I, 390; Zts. ang. Chem. 1909, **22**, 1810. D. R. P. 212501; abst. Mon. Sci. 1912, **77**, 179; Chem. Zentr. 1909, **80**, II, 665; Chem. Ztg. Rep. 1909, **33**, 445; Zts. ang. Chem. 1909, **22**, 1811. D. R. P. 212868, abst. Mon. Sci. 1912, **77**, 98; Chem. Zentr. 1909, **80**, II, 665; Chem. Ztg. Rep. 1909, **33**, 477; Chem. Zts. 1910, **9**, No. 1648; Jahr. Chem. 1909, **62**, I, 535; Wag. Jahr. 1909, **55**, I, 416; Zts. ang. Chem. 1909, **22**, 1811; Zts. Schiess. Spreng. 1909, **4**, 333. D. R. P. 219494; abst. C. A. 1910, **4**, 2032; Chem. Zentr. 1910, **81**, I, 971; Chem. Ztg. Rep. 1910, **34**, 142; Chem. Zts. 1910, **9**, No. 1924; Jahr. Chem. 1910, **63**, I, 584; Wag. Jahr. 1910, **56**, I, 471; Zts. ang. Chem. 1910, **23**, 1049; Zts. Schiess. Spreng. 1910, **5**, 175. D. R. P. 220539, 1909; abst. J. S. C. I. 1912, **31**, 565; Mon. Sci. 1914, **81**, 76; Chem. Zentr. 1910, **81**, I, 1397; Chem. Ztg. Rep. 1910, **34**, 179; Chem. Zts. 1910, **9**, No. 1876;

of the Badische Anilin & Soda Fabrik, succeeded in devising a furnace of comparatively simple and unique construction. He

Jahr. Chem. 1910, **63**, I, 588; Wag. Jahr. 1910, **56**, I, 480; Zts. ang. Chem. 1910, **23**, 1050; Zts. Schiess. Spreng. 1910, **5**, 175; C. A. 1910, **4**, 3125. D. R. P. 223026, 1909; abst. J. S. C. I. 1910, **29**, 879. C. A. 1910, **4**, 2987; Mon. Sci. 1914, **81**, 77; Chem. Zentr. 1910, **81**, II, 253; Chem. Ztg. Rep. 1910, **34**, 342; Jahr. Chem. 1910, **63**, I, 588; Wag. Jahr. 1910, **56**, I, 481; Zts. ang. Chem. 1910, **23**, 1961; Zts. Schiess. Spreng. 1910, **5**, 257. D. R. P. 223556, 1909; abst. Mon. Sci. 1914, **81**, 78; Chem. Zentr. 1910, **81**, II, 427; Chem. Ztg. Rep. 1910, **34**, 342; Chem. Zts. 1910, **9**, No. 2027; Jahr. Chem. 1910, **63**, I, 588; Wag. Jahr. 1910, **56**, I, 481; Zts. ang. Chem. 1910, **23**, 1901; Zts. Schiess. Spreng. 1910, **5**, 297. Addn. to D. R. P. 220539. D. R. P. 227012; abst. J. S. C. I. 1910, **29**, 1378; Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1910, **81**, II, 1345; Chem. Ztg. Rep. 1910, **34**, 543; Chem. Zts. 1911, **10**, No. 2264; Jahr. Chem. 1910, **63**, II, 1325; Wag. Jahr. 1910, **56**, I, 459; Zts. ang. Chem. 1910, **23**, 2337; Zts. Schiess. Spreng. 1910, **5**, 441. D. R. P. 229292; abst. Chem. Zentr. 1911, **82**, I, 177; Chem. Ztg. Rep. 1911, **35**, 11; Zts. ang. Chem. 1911, **24**, 86. D. R. P. 229780; abst. Mon. Sci. 1914, **81**, 84; Chem. Zentr. 1911, **82**, I, 274; Chem. Ztg. Rep. 1911, **35**, 43; Chem. Zts. 1911, **10**, No. 2373; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 281. D. R. P. 231805, 1909; abst. J. S. C. I. 1911, **30**, 421; Chem. Zentr. 1911, **82**, I, 852; Chem. Ztg. Rep. 1911, **35**, 127; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 565. D. R. P. 232926; abst. Chem. Zentr. 1911, **82**, I, 1089; Chem. Ztg. Rep. 1911, **35**, 223; Chem. Zts. 1912, **11**, No. 2621; Wag. Jahr. 1911, **57**, I, 467; Zts. ang. Chem. 1911, **24**, 856; Zts. Schiess. Spreng. 1911, **6**, 156. D. R. P. 233729, 1910; abst. J. S. C. I. 1911, **30**, 747; Chem. Zentr. 1911, **82**, I, 1388; Chem. Ztg. Rep. 1911, **35**, 271; Wag. Jahr. 1911, **57**, I, 466; Zts. ang. Chem. 1911, **24**, 949; Zts. Schiess. Spreng. 1911, **6**, 232. D. R. P. 233967; abst. Chem. Zentr. 1911, **82**, I, 1466; Chem. Ztg. Rep. 1911, **35**, 234; Wag. Jahr. 1911, **57**, I, 467; Zts. ang. Chem. 1911, **24**, 1003; Zts. Schiess. Spreng. 1911, **6**, 232. D. R. P. 235000, abst. Chem. Zentr. 1911, **82**, II, 170; Chem. Ztg. Rep. 1911, **35**, 321; Wag. Jahr. 1911, **57**, II, 46; Zts. ang. Chem. 1911, **24**, 1549. D. R. P. 235662, 1909; abst. J. S. C. I. 1911, **30**, 1058. D. R. P. 235765, 285766; abst. Chem. Zentr. 1911, **82**, II, 238, 239; Chem. Ztg. Rep. 1911, **35**, 342, 347; Wag. Jahr. 1911, **57**, I, 427; Zts. ang. Chem. 1911, **24**, 1443, 1444. D. R. P. 235868, abst. Mon. Sci. 1914, **81**, 204; Chem. Zentr. 1911, **82**, II, 239; Chem. Ztg. Rep. 1911, **35**, 363; Wag. Jahr. 1911, **57**, I, 428; Zts. ang. Chem. 1911, **24**, 1441. D. R. P. 236395, abst. Chem. Ztg. Rep. 1911, **35**, 374; Wag. Jahr. 1911, **57**, I, 428; Zts. ang. Chem. 1911, **24**, 1579. D. R. P. 237562, abst. Chem. Zentr. 1911, **82**, II, 812; Chem. Ztg. Rep. 1911, **35**, 438; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 1782; Zts. Schiess. Spreng. 1911, **6**, 354. D. R. P. 237796; abst. Chem. Zentr. 1911, **82**, II, 920; C. A. 1912, **6**, 1575; Chem. Ztg. Rep. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 461; Zts. ang. Chem. 1911, **24**, 1883. D. R. P. 238367; abst. C. A. 1912, **6**, 1887; Chem. Zentr. 1911, **82**, II, 1183; Chem. Ztg. Rep. 1911, **35**, 507; Wag. Jahr. 1911, **57**, I, 460; Zts. ang. Chem. 1911, **24**, 2028. D. R. P. 238368; abst. C. A. 1912, **6**, 1887; Chem. Zentr. 1911, **82**, II, 1183; Chem. Ztg. Rep. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 461; Zts. ang. Chem. 1911, **24**, 2029. D. R. P. 238369, 1909; abst. C. A. 1912, **6**, 1663; Chem. Zentr. 1911, **82**, II, 1077; Chem. Ztg. Rep. 1911, **35**, 529; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 2029; Zts. Schiess. Spreng. 1911, **6**, 411. D. R. P. 238958, abst. C. A. 1912, **6**, 2037; Chem. Zentr. 1911, **82**, II, 1392; Chem. Ztg. Rep. 1911, **35**, 547; Wag. Jahr. 1911, **57**, I, 642; Zts. ang. Chem. 1911, **24**, 2181. D. R. P. 239648, 1912; abst. J. S. C. I. 1913, **32**, 657; Wag. Jahr. 1911, **57**, I, 28; Zts. Ang. Chem. 1911, **24**, 2223. D. R. P. 239649, 1912; abst. J. S. C. I. 1913, **32**, 657; C. A. 1912, **6**, 2037; Chem. Zentr. 1911, **82**, II, 1497; Chem. Ztg. Rep.

found that a stable arc of great length could be indefinitely maintained in the axis of a tube along which a current of air is passed,

1911, **35**, 566; Wag. Jahr. 1911, **57**, I, 641; Zts. ang. Chem. 1911, **24**, 2274. D. R. P. 242288, 243839; abst. C. A. 1912, **6**, 2153, 2299; Chem. Zentr. 1912, **83**, I, 296, 865; Chem. Ztg. Rep. 1912, **36**, 43, 171; Wag. Jahr. 1912, **58**, I, 415, 457; Zts. ang. Chem. 1912, **25**, 328, 595; Zts. Schiess. Spreng. 1912, **7**, 185. D. R. P. 255732; abst. C. A. 1913, **7**, 1447; Chem. Zentr. 1913, **84**, I, 475; Chem. Ztg. Rep. 1913, **37**, 63; Wag. Jahr. 1913, **59**, I, 518; Zts. ang. Chem. 1913, **26**, 106. D. R. P. 265413, 1912; abst. J. S. C. I. 1913, **32**, 1068; C. A. 1914, **8**, 303; Chem. Zentr. 1913, **84**, II, 1436; Chem. Ztg. Rep. 1913, **37**, 590; Wag. Jahr. 1913, **59**, I, 523; Zts. ang. Chem. 1913, **26**, 630. D. R. P. 276133, 1912; abst. J. S. C. I. 1915, **34**, 27; Chem. Trade J. 1915, 575; Mon. Sci. 1917, **84**, 73; Chem. Zentr. 1914, **85**, II, 365; Chem. Ztg. Rep. 1914, **38**, 430; Wag. Jahr. 1914, **60**, I, 307; Zts. ang. Chem. 1914, **27**, 525. Aust. P. 34170, 34576, 40667, 1909; 51413, 51414. Swiss P. 44093, 44094, 1908; 46183, 51112. Swed. P. 34466. U. S. P. 911468, 1909; abst. J. S. C. I. 1907, **28**, 243; Mon. Sci. 1909, **71**, 141. U. S. P. 923012; abst. Mon. Sci. 1911, **75**, 99. U. S. P. 971501, 1910; abst. J. S. C. I. 1910, **29**, 949; Mon. Sci. 1913, **79**, 100; Chem. Ztg. Rep. 1911, **35**, 127. U. S. P. 991174, 991356; abst. Mon. Sci. 1912, **77**, 17. U. S. P. 993144, 1909; abst. J. S. C. I. 1910, **29**, 424; Mon. Sci. 1912, **77**, 18. U. S. P. 1003279, 1006206, 1910; abst. J. S. C. I. 1911, **30**, 26; C. A. 1912, **6**, 140; Mon. Sci. 1912, **77**, 129; Chem. Ztg. Rep. 1911, **35**, 591. U. S. P. 1013984; abst. C. A. 1912, **6**, 671; Mon. Sci. 1912, **77**, 130. U. S. P. 1022351; abst. C. A. 1912, **6**, 1661; J. Soc. Dyers Col. 1912, **28**, 199; Mon. Sci. 1912, **77**, 135. U. S. P. 1027312, 1910; abst. J. S. C. I. 1911, **30**, 86; C. A. 1912, **6**, 1964; Mon. Sci. 1912, **77**, 132. U. S. P. 1029528; abst. J. S. C. I. 1910, **29**, 1010; C. A. 1912, **6**, 2500; Mon. Sci. 1912, **77**, 133; Chem. Ztg. Rep. 1912, **36**, 405. U. S. P. 1039325; abst. C. A. 1912, **6**, 3499; Mon. Sci. 1913, **79**, 6. U. S. P. 1043798; abst. C. A. 1913, **7**, 220. U. S. P. 1046212; abst. C. A. 1913, **7**, 563; Chem. Ztg. Rep. 1913, **37**, 190. U. S. P. 1053951, 1911; abst. J. S. C. I. 1912, **31**, 385; C. A. 1913, **7**, 1268; Mon. Sci. 1913, **79**, 145. U. S. P. 1053952, 1911; abst. J. S. C. I. 1912, **31**, 1057; C. A. 1913, **7**, 1268; Mon. Sci. 1913, **79**, 145. U. S. P. 1068966, 1068967, 1068968, 1068969, 1911; abst. J. S. C. I. 1911, **30**, 1115; C. A. 1913, **7**, 3203; Mon. Sci. 1914, **81**, 16. U. S. P. 1083585, 1911; abst. J. S. C. I. 1912, **31**, 432; C. A. 1914, **8**, 994; Mon. Sci. 1914, **81**, 65. U. S. P. 1086130, 1912; abst. J. S. C. I. 1913, **32**, 1010; C. A. 1914, **8**, 1193; Mon. Sci. 1914, **81**, 97. U. S. P. 1089185, 1912; abst. J. S. C. I. 1913, **32**, 233; C. A. 1914, **8**, 1490. U. S. P. 1094182, 1913; abst. J. S. C. I. 1914, **33**, 549; C. A. 1914, **8**, 2039; Mon. Sci. 1914, **81**, 137. U. S. P. 1094194, 1910; abst. J. S. C. I. 1911, **30**, 1012; C. A. 1914, **8**, 2039; Mon. Sci. 1914, **81**, 137. U. S. P. 1095425, 1095426, 1095427; abst. C. A. 1914, **8**, 2119; Mon. Sci. 1914, **81**, 141. U. S. P. 1118628, 1915; abst. J. S. C. I. 1915, **34**, 29; Mon. Sci. 1915, **82**, 18. Add. dated May 24, 1912, to F. P. 425099, abst. J. S. C. I. 1912, **31**, 1125; C. A. 1912, **6**, 1969; Chem. Ztg. Rep. 1911, **35**, 342. U. S. P. 1128530, 1912; abst. J. S. C. I. 1912, **31**, 922. U. S. P. 1128843, 1912; abst. J. S. C. I. 1912, **31**, 1031. U. S. P. 1140510, 1912; abst. J. S. C. I. 1912, **31**, 721. U. S. P. 1148570, 1910; abst. J. S. C. I. 1911, **30**, 1012. U. S. P. 1152930, 1915; abst. J. S. C. I. 1915, **34**, 1055. F. P. 425099, 1910; abst. J. S. C. I. 1915, **34**, 1055; C. A. 1912, **6**, 1969; Chem. Ztg. Rep. 1911, **35**, 342. U. S. P. 1158167, 1911; abst. J. S. C. I. 1912, **31**, 432. U. S. P. 1202995, 1909; abst. J. S. C. I. 1910, **29**, 498; J. S. C. I. 1916, **35**, 1218. U. S. P. 1211394, abst. J. S. C. I. 1916, **35**, 215. E. P. 5688, 1904; abst. J. S. C. I. 1905, **24**, 201. E. P. 26602, 1904; abst. J. S. C. I. 1915, **24**, 1178. E. P. 14955, 1905; abst. J. S. C. I. 1906, **25**, 890. E. P. 9279, 1906; abst. J. S. C. I. 1907, **26**, 54. E. P. 2414, 1908; abst. J. S. C. I. 1908, **27**, 809; 1909, **28**, 243. E. P. 10867, 1908; abst. J. S. C. I. 1909, **28**, 656. E. P. 20406,

the stability of the arc being materially increased by imparting the air a vortical motion. From the present exhaustive trials,

1908; abst. J. S. C. I. 1909, **28**, 509, 939. E. P. 2525, 1909; abst. J. S. C. I. 1909, **28**, 309. E. P. 10465, 1909; abst. J. S. C. I. 1910, **29**, 423. E. P. 10867, 1909; abst. J. S. C. I. 1910, **29**, 425; Chem. Ztg. Rep. 1910, **34**, 315. E. P. 11274, 1909; abst. J. S. C. I. 1910, **29**, 757. E. P. 17642, 1909. F. P. 411446; abst. J. S. C. I. 1910, **29**, 949, 1250. E. P. 17951, 1909. F. P. 406943; abst. J. S. C. I. 1910, **29**, 488, 1057. E. P. 20129, 1909; abst. J. S. C. I. 1910, **29**, 695. E. P. 20502, 22715, 1909; abst. J. S. C. I. 1910, **29**, 1167. E. P. 30380, 1909; abst. J. S. C. I. 1910, **29**, 950. E. P. 30502, 1909. F. P. 411674; abst. J. S. C. I. 1910, **29**, 949, 1455. E. P. 30503, 1909; abst. J. S. C. I. 1910, **29**, 949. F. P. 411674; abst. J. S. C. I. 1911, **30**, 87. E. P. 5382, 1910. F. P. 418059; abst. J. S. C. I. 1911, **30**, 26, 489. E. P. 10441, 1910; abst. J. S. C. I. 1911, **30**, 87. F. P. 416877, 1910; abst. J. S. C. I. 1910, **29**, 1378. E. P. 13097, 1910. F. P. 418434; abst. J. S. C. I. 1911, **30**, 85, 748. E. P. 14023, 15973, 1910. F. P. 418287; abst. J. S. C. I. 1911, **30**, 85, 957; 1910, **29**, 1453. E. P. 16368, 1910. F. P. 418425; abst. J. S. C. I. 1911, **30**, 86, 362. E. P. 19249, 19250, 19251, 1910; F. P. 425099; abst. J. S. C. I. 1911, **30**, 1012, 1116; C. A. 1912, **6**, 1346; Chem. Ztg. Rep. 1911, **35**, 575. E. P. 19250, 1910; abst. J. S. C. I. 1911, **30**, 1012. E. P. 19251, 1910; abst. J. S. C. I. 1911, **30**, 1012; Chem. Ztg. Rep. 1911, **35**, 575. E. P. 19778, 1910. F. P. 429696; abst. J. S. C. I. 1911, **30**, 1211, 1253. E. P. 20127, 1910; abst. J. S. C. I. 1911, **30**, 747. E. P. 61, 1911; abst. J. S. C. I. 1911, **30**, 1057; J. Soc. Dyers Col. 1911, **27**, 241. E. P. 5833, 1911; abst. J. S. C. I. 1911, **30**, 1115; C. A. 1912, **6**, 2500. E. P. 5834, 1911; abst. J. S. C. I. 1911, **30**, 1115. E. P. 5835, 1911; abst. J. S. C. I. 1911, **30**, 1115; C. A. 1912, **6**, 2500. E. P. 5836, 1911; abst. J. S. C. I. 1911, **30**, 1115. E. P. 21151, 1911; abst. J. S. C. I. 1912, **31**, 1031; C. A. 1913, **7**, 1083. E. P. 24657, 1911. F. P. 436472; abst. C. A. 1913, **7**, 404; J. S. C. I. 1912, **31**, 432, 817; Chem. Ztg. Rep. 1912, **36**, 581. E. P. 25252, 1911. F. P. 436472; abst. C. A. 1913, **7**, 1589; J. S. C. I. 1912, **31**, 432, 923. E. P. 26749, 1911; abst. J. S. C. I. 1912, **31**, 385; C. A. 1913, **7**, 1789; Chem. Ztg. Rep. 1912, **36**, 390. E. P. 28167, 1911. F. P. 425099; abst. J. S. C. I. 1912, **31**, 1125; 1913, **32**, 85; C. A. 1913, **7**, 1958. E. P. 3345, 1912; abst. J. S. C. I. 1912, **31**, 1031; C. A. 1913, **7**, 2668. E. P. 8617, 1912; F. P. 444455; abst. J. S. C. I. 1912, **31**, 1126; 1913, **32**, 289; C. A. 1913, **7**, 2838. E. P. 9841, 1912; F. P. 432472; abst. C. A. 1913, **7**, 3533; J. S. C. I. 1912, **31**, 432; 1913, **32**, 289. E. P. 9842, 1912; F. P. 431295; abst. J. S. C. I. 1913, **32**, 233, 289; C. A. 1913, **7**, 2838. E. P. 22352, 1912; abst. J. S. C. I. 1913, **32**, 487, 868; C. A. 1914, **8**, 996. E. P. 25259, 25260, 1912; abst. J. S. C. I. 1913, **32**, 909, 1155; C. A. 1914, **8**, 407, 1498; Chem. Ztg. Rep. 1913, **37**, 634. E. P. 26770, 1942; abst. J. S. C. I. 1914, **33**, 22; C. A. 1914, **8**, 1649; Chem. Ztg. Rep. 1914, **38**, 128. E. P. 28200, 1912; abst. J. S. C. I. 1913, **32**, 1009; C. A. 1914, **8**, 1859. E. P. 29260, 1912; abst. J. S. C. I. 1913, **32**, 1010; C. A. 1914, **8**, 996; Chem. Ztg. Rep. 1913, **37**, 695. E. P. 9263, 1913; F. P. 464237; abst. J. S. C. I. 1914, **33**, 549, 593; C. A. 1914, **8**, 3355. E. P. 9654, 1913; F. P. 458951; abst. J. S. C. I. 1913, **32**, 1155. E. P. 12977, 1913; abst. J. S. C. I. 1914, **33**, 483; C. A. 1914, **8**, 3842. E. P. 13258, 1913; abst. J. S. C. I. 1913, **32**, 1010. E. P. 24823, 1913; F. P. 466303; abst. J. S. C. I. 1914, **33**, 645, 750. E. P. 13687, 1914; abst. J. S. C. I. 1915, **34**, 961. E. P. 13848, 1914; abst. J. S. C. I. 1915, **34**, 799. E. P. 1358, 1915; abst. J. S. C. I. 1916, **35**, 689. E. P. 7651, 1915; abst. J. S. C. I. 1916, **35**, 1015. E. P. 13297, 1915; abst. J. S. C. I. 1916, **35**, 1108. E. P. 13298, 1915; abst. J. S. C. I. 1916, **35**, 1015. F. P. 350392; abst. J. S. C. I. 1905, **24**, 1178; Zts. Elektrochem. 1906-1907, **13**, 214; Mon. Sci. 1911, **75**, 573. F. P. 357358, 1911; abst. J. S. C. I. 1911, **30**, 905; Mon. Sci. 1911, **75**, 571, 572. F. P. 363643; abst. Mon. Sci. 1907, **67**, 92. F. P. 372714, 1909; abst. Mon. Sci. 1908, **69**, 82; Chem. Ztg.

it, would now appear that this furnace is destined to win recognition as an even more efficient device than that of K. Birkeland and S. Eyde. The fundamental patent of Schönherr¹

Rep. 1907, **31**, 207. F. P. 387001; abst. Mon. Sci. 1909, **71**, 109; Chem. Ztg. Rep. 1908, **32**, 412. F. P. 387002; abst. J. S. C. I. 1908, **27**, 809; Mon. Sci. 1909, **71**, 109. India P. Appl. 26, 1904. F. P. 396375; abst. J. S. C. I. 1909, **28**, 599; C. A. 1911, **5**, 357; Mon. Sci. 1910, **73**, 161; Chem. Ztg. Rep. 1909, **33**, 311. F. P. 398738, 1909; abst. J. S. C. I. 1909, **28**, 884; Mon. Sci. 1910, **73**, 163; Chem. Ztg. Rep. 1909, **33**, 366. F. P. 405712, 1909; abst. J. S. C. I. 1910, **29**, 424, 950; Mon. Sci. 1910, **73**, 172; Chem. Ztg. Rep. 1910, **34**, 63. F. P. 406943, 1909; abst. J. S. C. I. 1910, **29**, 488; Mon. Sci. 1910, **73**, 175; 1914, **81**, 152; Chem. Ztg. Rep. 1910, **34**, 126. F. P. 410710, 411446, 1910; abst. J. S. C. I. 1910, **29**, 949; C. A. 1912, **6**, 1965; Mon. Sci. 1913, **79**, 74; Chem. Ztg. Rep. 1910, **34**, 415. F. P. 411574; abst. Mon. Sci. 1911, **75**, 170. F. P. 411674; abst. J. S. C. I. 1910, **29**, 494, 949; Mon. Sci. 1913, **79**, 75; C. A. 1912, **6**, 1965; Chem. Ztg. Rep. 1910, **34**, 415. F. P. 412788, 1910; abst. J. S. C. I. 1910, **29**, 1010; 1911, **30**, 684; C. A. 1912, **6**, 1965; Mon. Sci. 1913, **79**, 76; Chem. Ztg. Rep. 1910, **34**, 481; 1911, **35**, 306. F. P. 413421, 1910; abst. J. S. C. I. 1910, **29**, 1117. F. P. 416877, 1910; abst. J. S. C. I. 1913, **79**, 1378; C. A. 1912, **6**, 1966; Mon. Sci. 1913, **79**, 83; Chem. Ztg. Rep. 1910, **34**, 632. F. P. 417490, 1910; abst. J. S. C. I. 1911, **30**, 26; C. A. 1912, **6**, 1999; J. Soc. Dyers Col. 1910, **26**, 260; 1912, **28**, 332; Chem. Ztg. Rep. 1911, **35**, 86. F. P. 418059; 1910; abst. J. S. C. I. 1911, **30**, 26; Mon. Sci. 1913, **79**, 85. F. P. 418287; 1910; abst. J. S. C. I. 1911, **30**, 85; Mon. Sci. 1913, **79**, 86. F. P. 418425; abst. Mon. Sci. 1913, **79**, 86. F. P. 418434; 1910; abst. J. S. C. I. 1911, **30**, 85. F. P. 418825; 1910; abst. J. S. C. I. 1911, **30**, 86. F. P. 418892; abst. J. S. C. I. 1910, **29**, 1167. F. P. 425099; 1910; abst. J. S. C. I. 1911, **30**, 1012, 1125; 1915, **34**, 1055; C. A. 1912, **6**, 1969; Chem. Ztg. Rep. 1911, **35**, 342. U. S. P. 1152930, J. S. C. I. 1915, **34**, 1055. Addn. dated May 24, 1912, to F. P. 425099; abst. J. S. C. I. 1912, **31**, 1125; U. S. P. 1118628, 1914; abst. J. S. C. I. 1915, **34**, 29; Mon. Sci. 1915, **82**, 18. F. P. 429696; 1911; abst. J. S. C. I. 1911, **30**, 1211; Mon. Sci. 1913, **79**, 126; Chem. Ztg. Rep. 1912, **36**, 57. F. P. 431295, 1911; abst. J. S. C. I. 1911, **30**, 1381; 1913, **32**, 233, 657; Mon. Sci. 1913, **79**, 129. F. P. 436472, 1911; abst. J. S. C. I. 1912, **31**, 432; Mon. Sci. 1913, **79**, 133. F. P. 436680, 1911; abst. J. S. C. I. 1912, **31**, 385; Mon. Sci. 1913, **79**, 134. F. P. 439261, 1912; abst. J. S. C. I. 1912, **31**, 721; Mon. Sci. 1913, **79**, 137. F. P. 441695, 1912; abst. J. S. C. I. 1912, **31**, 922; 1913, **32**, 142. F. P. 444455, 1912; abst. J. S. C. I. 1912, **31**, 1126. F. P. 449010, 1912; abst. J. S. C. I. 1913, **32**, 487; C. A. 1913, **7**, 2839; Mon. Sci. 1914, **81**, 4; Chem. Ztg. Rep. 1913, **37**, 247. F. P. 456963, 1912; abst. J. S. C. I. 1913, **32**, 1009; C. A. 1914, **8**, 409; Chem. Ztg. Rep. 1913, **37**, 634. F. P. 458218, 1912; abst. J. S. C. I. 1913, **32**, 1010; Chem. Ztg. Rep. 1913, **37**, 695. F. P. 458950, 1912; abst. J. S. C. I. 1913, **32**, 909; Mon. Sci. 1914, **81**, 72. F. P. 458951, 1913; abst. J. S. C. I. 1913, **32**, 1155. F. P. 464327, 1913; abst. J. S. C. I. 1914, **33**, 549. F. P. 466303, 1913; abst. J. S. C. I. 1914, **33**, 645; Mon. Sci. 1916, **83**, 14; Chem. Ztg. Rep. 1914, **38**, 547. See also A. Bernthsen, 8th Intl. Cong. Appl. Chem. 1912; abst. J. S. C. I. 1912, **31**, 982; C. A. 1912, **6**, 3497. ¹ Perkins, Chem. Eng. 1913, **18**, 238; abst. C. A. 1914, **8**, 1061. O. Schönherr, Zts. ang. Chem. 1908, **21**, 1633; Trans. Amer. Electrochem. Soc. 1909, **16**, 131; Chem. Zentr. 1908, **79**, 11, 1136; Wag. Jahr. 1908, **54**, 1, 426; C. A. 1909, **3**, 1619. F. Haber, Australia P. 19327, 1910. D. R. P. 48100, 1909. R. Wiegolaski, U. S. P. 1054886, 1061892; abst. C. A. 1913, **7**, 2163. E. P. 2165, 2214, 1913; abst. J. S. C. I. 1913, **32**, 432, 665, 1076. F. Wiegolaski and A. Schönherr, U. S. P. 1028516; abst. J. S. C. I. 1910, **29**, 1117.

1. D. R. P. 201279, 1905; Chem. Zentr. 1908, **79**, 1, 1139; Chem. Ztg. Rep. 1908, **32**, 532; Chem. Zts. 1908, **7**, No. 1012; Jahr. Chem. 1905-

was issued in 1905 and rather than being an elaboration and perfection of the essential features of the Norwegian invention, possesses many thoroughly unique and fundamental principles of basic merit. In place of the great disk of electric flame, he develops a long, slender arc confined in the axis of a narrow iron tube, as shown in illustration in Fig. 68 and in section in Fig. 69, through which a current of air is forced.

The Schönherr furnace now in use comprizes a somewhat slender vertical column of iron plate 23 feet in height, lined with a refractory non-conductor, three concentric tubes of iron being in the center core. The inner tube, 6 inches or less in diameter, is the reaction chamber; the others forming channels for the entrance of the air current, and for its exit after coming in contact with the arc. The arrangement is such that a large proportion of the heat in the outgoing stream of gas is imparted to the incoming current.

At the lower extremity of the reaction tube is an iron bar serving as the main electrode, movable in a vertical direction through an opening in one terminal of the electric current. The copper terminal is hollow, permitting the circulation of a supply of cold water, so adjusted as to prevent an undue rise of temperature. The adjustable iron electrode projects slightly above the surface of the terminal, and is raised a little from time to time as the end is worn away by the arc. The electrodes when in active use are said to last about three months, it being but a matter of a few minutes to substitute a new electrode for an old one. The electrode cost is said to be less than two cents per kilowatt year.

The iron reaction tube fulfils the function of the second electrode, and is in direct connection with the inclosing tubes and the other metallic parts of the furnace and the element of danger is minimized by grounding the entire system. By means of a lever the space between the main electrode and the lower extremity of the tube can be bridged over by a metallic connection and the arc be formed. The same device permits of a re-lighting in the usual case of arc being extinguished.¹

A distinctive and novel feature in the furnace is the process, 1908, I, 1772, 1909, **62**, 529; Wag. Jahr. 1908, **54**, I, 410; Zts. ang. Chem. 1908, **21**, 2330.

1. F. Haber and A. Koenig, Zts. Elektrochem. 1910, **16**, 11; abst.

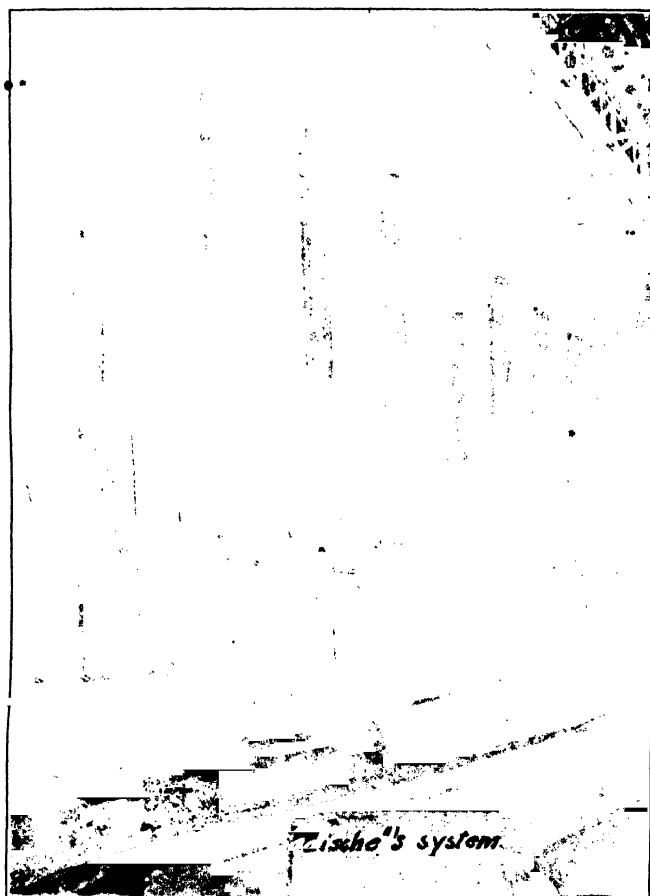


FIG. 68.—SCHÖNHERR FURNACES, BADISCHE SYSTEM

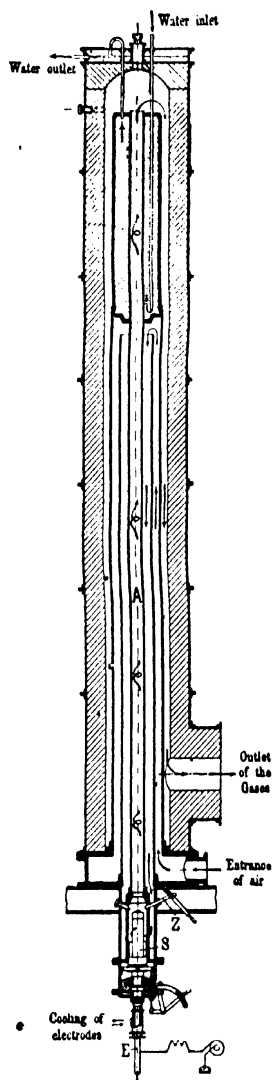


FIG. 69.—SCHÖNHERR FURNACE

vision for the admission of air. The air current, forced by a powerful aspirator, enters the lower part of the circular space between the two outer tubes. The larger tube is heated by a current of the gaseous products of the operation passing downward through the channel lying between it and the external walls of the furnace. The upward passageway of the entering current terminates at two-thirds of the height of the reaction tube, and the air, already heated to some extent, descends by the inner circular channel, in immediate contact with the hot walls of the reaction tube, to its lower extremity. Here it enters the chamber, or space, containing the main electrode. The entry is through a number of small openings arranged in several horizontal rows in the sides of this circular chamber. The orifices are tangential to the walls of the chamber. The current of gas then passes through the reaction tube, issues from its upper extremity, and descends in the external circular passageway already mentioned. A water jacket surrounds the upper third of the reaction tube. Small windows, protected by mica, allow a view of the chamber containing the main electrode, and also of the space immediately above the reaction tube.

The kindling of the arc is brought about by pressure on an external lever, which causes a metallic bar to slip into position between the main electrode and the lower end of the reaction tube. As the bar is connected electrically to the latter it acts temporarily as a second electrode and the arc springs into existence. Various other methods have also been used successfully. A moistened shaving of wood introduced into the free space suffices to so increase the conductivity of the air that the discharge can take place. Or a small flame directed into the open space will heat the air sufficiently to raise its conductivity to the point at which an arc can bridge over the space between the electrodes. A block of wood wound with wire has also been employed; and the discharge of a blank pistol cartridge into the chamber will likewise bring about the desired result.

The arc springs into activity in the midst of a rapidly mov-

C. A. 1910, **4**, 717; Chem. Zentr. 1910, **81**, I, 694. O. Schönherr, Trans. Amer. Electrochem. Soc. 1909, **16**, 131; Elektrotechn. Zts. 1909, **30**, 366, 397; C. A. 1909, **3**, 1619; 1910, **4**, 1131, 1940; Chem. Eng. 1910, **11**, 129. E. Scott, J. S. **Q.** 1. 1915, **34**, 113; Smithsonian Reports, 1913, 359; Chem. Trade J. 1915, **56**, 43; abstr. C. A. 1915, **9**, 1273, 1274.

ing current of air. As a result it is swiftly drawn upward, so that it forms a slender column of flame occupying the axis of the reaction tube for its entire length. It is intensely luminous, but burns quietly and noiselessly. The flame does not come in contact with the reaction tube except at its upper extremity. A second electrode can be stationed near the top, in which case it is not necessary that the reaction chamber tube should be of metal. The initial lighting is accomplished by introducing a wire momentarily between the two electrodes. These long constant flames are of the greatest interest to physicists, as hitherto arcs of any considerable length have been of uncertain duration. With a tension of less than 4,000 volts, Schönherr has secured columns of flame 26 feet in length; greater lengths can probably be produced. For technical purposes a flame of 23 feet seems to be the most practical. The movement of the ascending column of air in the reaction tube is a feature of dominating importance. It enters the chamber about the lower electrode under a pressure of 50 to 100 centimeters of water and is raised to a temperature of 500° C. by the heat transmitted by the outgoing current. A higher temperature does not seem safe in an apparatus constructed of wrought iron, and the movement of the current is adjusted so as to prevent overheating. It is, however, the rapidity of movement that controls the length of the flame and it must not fall below a certain rate. The chief peculiarity of this flame results from the method of its introduction into the electrode chamber, i. e., tangentially through a number of small openings; the total section of these openings is less than that of the circular canal conducting the air, thus insuring a uniform pressure in the numerous minute currents on entering the chamber. As a result a very pronounced vortical motion is imparted to the entire ascending column of air, a motion so strong that there is a material difference in pressure between the axis of the vortex, occupied by the column of flame and the outer sections of the current. As the air nears the top of the tube, the spiral motion gradually loses its intensity and the characteristics of a gaseous vortex are less pronounced. Numerous variations in the manner of introducing the air current have been tested. Fairly good results have been secured by admitting it above the main electrode; it has also been admitted directly into the reaction tube through small

orifices or slits of different shapes and positions. The controlling factor is the production of the pronounced vortical motion. A slight deviation from the horizontal location of the openings, as described, seems favorable for this purpose.

The best results have followed a somewhat more complicated system of introducing the air. By forcing hot air into the lower chamber immediately above the electrode, and cold air a little higher up, it is possible to create a vortical column, the center of which is much hotter than the inclosing strata. There are certain evident advantages in this arrangement for producing a maximum effect in the chemical reaction. In a recent patent (German patent 229292) the "Badische" company proposes to impart a spiral motion, in opposite directions, to the two columns—the central "core" and the inclosing mantle.

The reaction is identical with that obtained in the Birkeland and Eyde furnace. The union of nitrogen and oxygen to form nitric oxide takes place in contact with the electric flame. As the products escape from the zone of great heat into the colder outer portions of the current the temperature falls so rapidly that the reverse reaction (the splitting up of nitric oxide into its constituents) is prevented to a notable degree. This quick cooling, which is all-important in securing a good yield, is further facilitated by inclosing the upper third of the tube with a water jacket. The net result is that the air current issues from the top of the reaction tube with a temperature of only 1200° C., and that the amount of nitric oxide present, as a product of the brief contact with the arc, is materially above 2%, reaching even at times, it is claimed, 2.5%. As compared with a Birkeland and Eyde furnace, the Schönherr device, apart from its somewhat higher yield, is characterized by its simplicity of construction and its durability. There are no movable parts, except of necessity the lower electrode, there is no costly electromagnet, and use is made of ordinary iron piping in building a furnace. The degree of safety in operating such a furnace is marked.

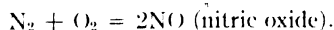
In one respect Schönherr boldly differed from the accepted rules for securing a maximum yield of nitric oxide. Instead of aiming to have a given volume of air remain momentarily in contact with the arc and then come into a zone of colder air or pass over a chilled surface, he forces the entire volume to remain

for a measurable length of time within the range of activity of the arc, while passing the entire distance through the long narrow reaction tube. The same end is attained, however, and apparently somewhat more successfully, by imparting a vortical movement to the ascending air column (with its resultant lowering of pressure in the center), by cooling the lower section of the reaction tube with the help of the inflowing current, and by cooling to a still greater degree the upper section of the tube with the aid of water. This means, of course, that temperatures fall very rapidly between the arc and the walls of the tube. It should be mentioned in this connection that Prof. Guye, in his experiments with a Schönherr tube, finds that the immobility of the long arc is not due to the vortical motion of the air current. The flame is quite as stable when air enters freely at the lower end of the reaction tube. This property he attributes rather to the increased viscosity of air at the high temperature prevailing in the center of the arc. An increase of $500^{\circ}\text{C}.$ in temperature means a quintupling of the viscosity of nitrogen.

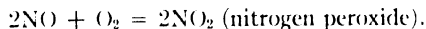
Schönherr has rightly pointed out that for the maximum continuous formation of nitrous gases by the action of high temperatures under ordinary circumstances, the highly heated air must be rapidly cooled.

The chemistry involved in the process, and in general in the Birkeland-Eyde and Pauling processes is as follows:

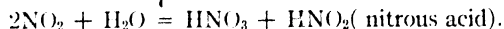
In the electric furnace from 3000° down to 1000° nitric oxide, a colorless gas, is formed—



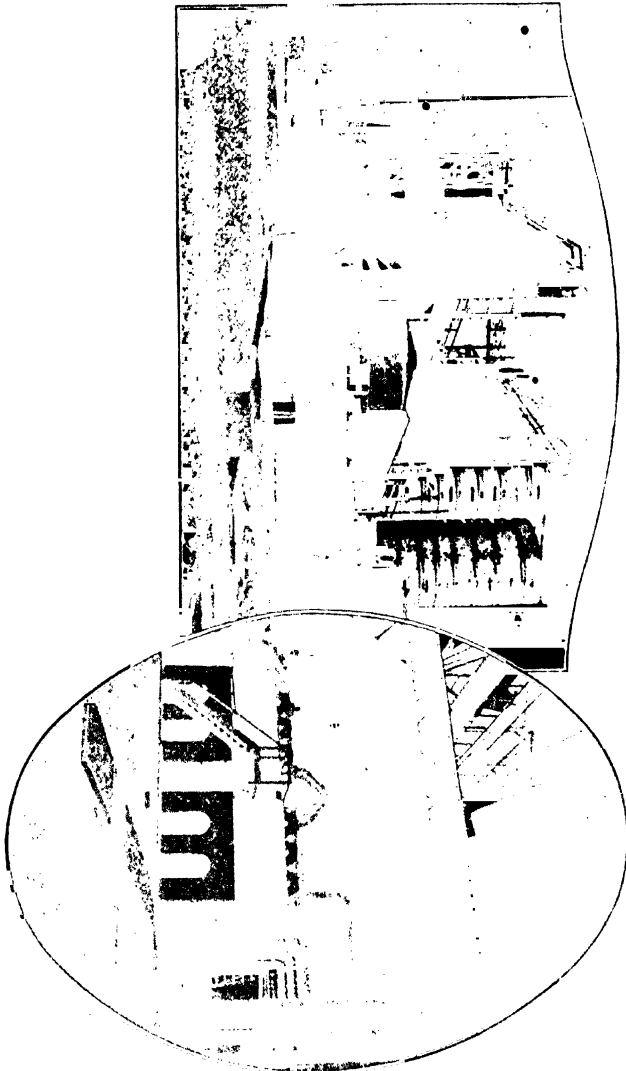
In the oxidation chambers, etc., from 500° down to 50° , the red-brown gas nitrogen peroxide is formed—



In the four acid absorption towers the nitrogen peroxide combines with water to form nitric acid and nitrous acid—



As the nitrous acid is unstable in an aqueous solution it gives nitric acid and nitric oxide—



FIGS. 70 AND 71.—SYNTHETIC NITRIC ACIDS (POUDRERIE NATIONALE D'ANGOULEME)

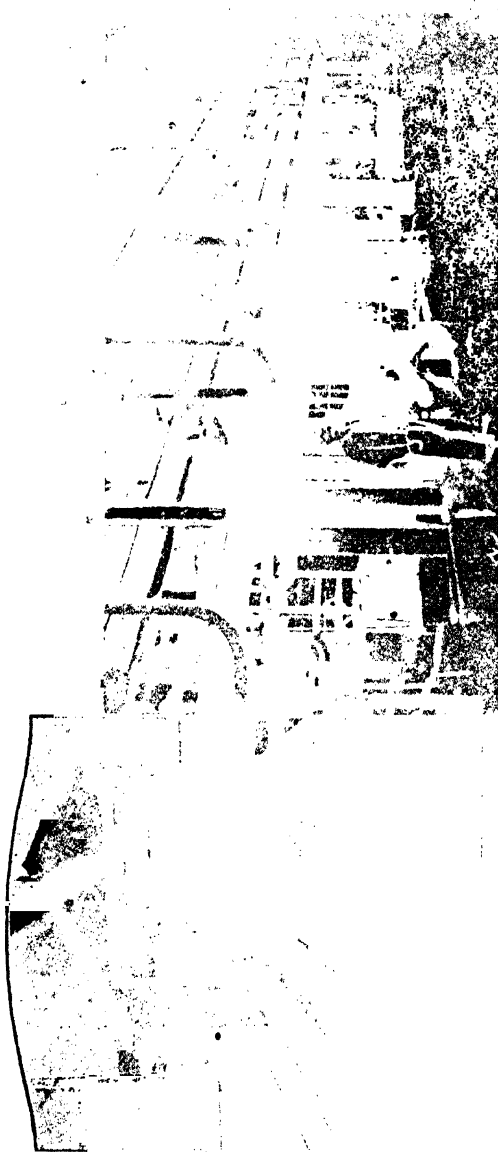
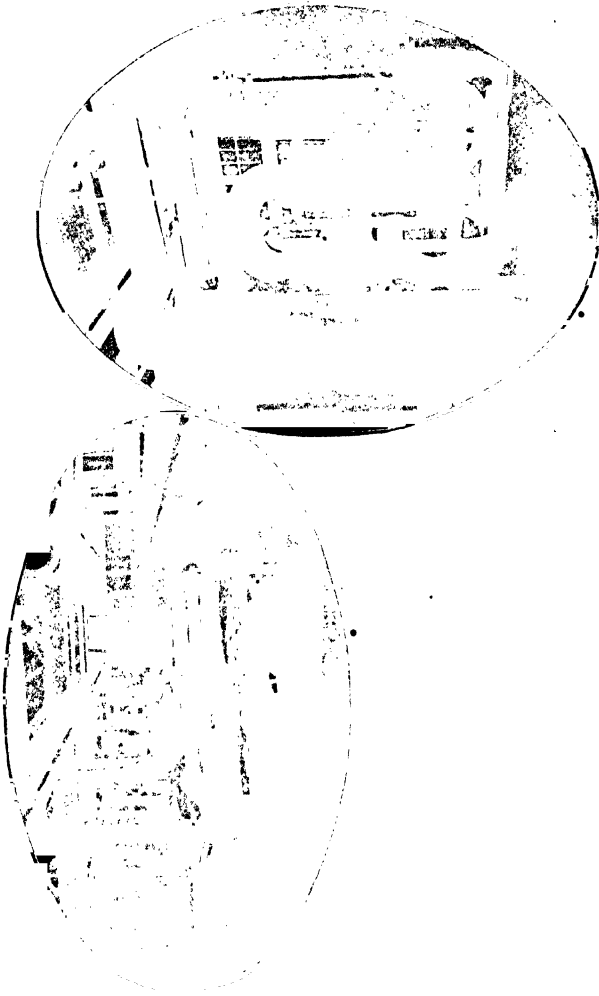
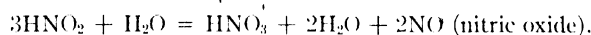


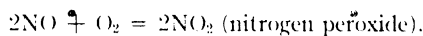
FIG. 72.—TRANSPORTATION OF CYANAMIDE
SYNTHETIC NITRIC ACID (POUDRIERIE NATIONALE D'ANGOULÊME)
FIG. 73.—AUTOCLAVES



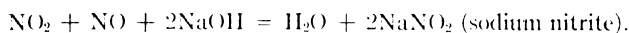
FIGS. 74 AND 75.—SYNTHESIS OF AMMONIA FROM THE AIR



The nitric oxide then combines with more oxygen to form again nitrogen peroxide, and the above equations are repeated



What is left of the nitrogen peroxide and nitric oxide gases pass to the fifth tower, when they meet sodium hydroxide to form sodium nitrite—



The nitric acid of 40% solution is sprayed onto calcium car-

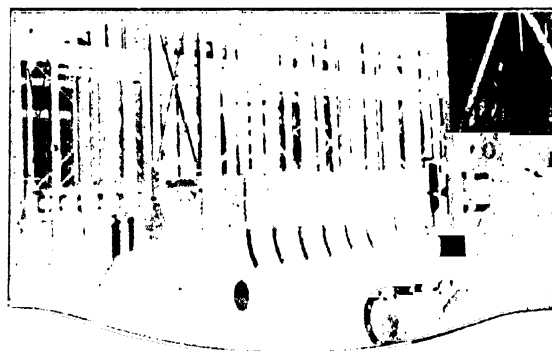
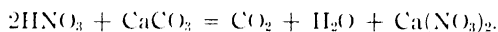


FIG. 76.—CATALYZERS FOR SYNTHETIC NITRIC ACID MANUFACTURE

bonate, and the carbon dioxide gas is driven off, leaving calcium nitrate



The solution is then pumped into solidification pans, under which cold air is circulated to accelerate cooling, and the nitrate of lime stiffens into a brittle, crystalline mass. This is broken up into lumps, which pass to ball crushing mills, where it is reduced to a granular state. The coarse powder is then raised by an elevator into a hopper, from the bottom of which it falls into barrels which hold two hundred-weight. These barrels are lined with paper to guard against damp.

K. Birkeland and S. Eyde Nitric Acid Process.¹ These inventions relate to a series of processes² for the treatment of mixtures of gases for obtaining a combination of atmospheric oxygen and nitrogen in the formation of nitric acid and nitrates, and as a commercial proposition, has been highly successful. The essence

1. K. Birkeland, *Trans. Faraday Soc.* 1906, **2**, 98; *Electrochem. Metall. Ind.* 1906, **4**, 295. *L'Industria Chimica*, **7**, 45; abst. *C. A.* 1907, **1**, 1460. K. Birkeland and S. Eyde, *Chem. Ztg. Rep.* 1907, **31**, 84; 1909, **33**, 562. K. Birkeland and S. Garfield, *Met. Chem. Eng.* 1911, **9**, 436. F. Bühler, *Chem. Ind.* 1911, **34**, 210. N. Busvold, *Chem. Ztg.* 1914, **38**, 799. A. Crossley, *Zts. Electrochem.* 1905, **11**, 252. *Anon. Engineering*, 1909, **88**, 611. E. Dingslage, *Chem. Ztg.* 1911, **35**, 1045. S. Eyde, *Chem. Ztg.* 1909, **33**, 266; 1912, **36**, 1032; *J. Roy. Soc. Arts*, 1909, **57**, 565; *J. S. C. I.* 1909, **28**, 1214. *J. Ind. Eng. Chem.* 1912, **4**, 771. *Chem. Engr.* 1912, **16**, 188. G. Flusin, *Chem. Ind.* 1914, **37**, 525. P. Frankland, *J. S. C. I.* 1915, **34**, 310; *Zts. ang. Chem.* 1915, **28**, III, 366. F. Haber and A. Koenig, *Zts. Elektrochem.* 1910, **16**, 11. S. Hale, *Chem. Ztg.* 1911, **35**, 1130. W. Herman, *Chem. Ztg.* 1913, **37**, 918. W. Landis, *J. Ind. Eng. Chem.* 1913, **7**, 433; 1916, **8**, 156. *Met. Chem. Eng.* 1915, **13**, 213; 1916, **14**, 260. *Maizieres, Engrais*, **26**, 1301; abst. *C. A.* 1912, **6**, 1343. F. Mason, *Mining. Sci. Press* 1916, **113**, 265; abst. *C. A.* 1916, **10**, 2619. E. Perkins, *Chem. Eng.* **18**, 238; *Chem. Ind.* 1914, **37**, 221. E. Scott, *Nature*, 1912, **89**, 463; abst. *J. Ind. Eng. Chem.* 1912, **4**, 619. A. Stutzer and S. Goy, *Chem. Ztg.* 1911, **35**, 891; *Chem. Ind.* 1912, **35**, 69. E. Scott, *J. S. C. I.* 1915, **34**, 114; *J. Soc. Arts*, 1912, **60**, 156. F. Washburn, *Trans. Am. Electrochem. Soc.* 1915, **27**, 385. *Met. Chem. Eng.* 1915, **13**, 309. O. Witt, *Chem. Ind.* 1905, **28**, 703; *Chem. Trade J.* 1911, **48**, 454; 1911, **49**, 632; abst. *Chem. Centr.* 1906, **77**, I, 409.
2. E. P. 20049, 1903. E. P. 20003, 1904; abst. *J. S. C. I.* 1905, **24**, 34. E. P. 28613, 1904; abst. *J. S. C. I.* 1905, **24**, 619. E. P. 28614, 1904; abst. *J. S. C. I.* 1905, **24**, 619. E. P. 335329, 1903; abst. *J. S. C. I.* 1904, **23**, 193. E. P. 3525, 1905; abst. *J. S. C. I.* 1905, **24**, 895; *Zts. ang. Chem.* 1905, **18**, 1848. E. P. 16885, 1907; abst. *J. S. C. I.* 1908, **27**, 447. E. P. 25632, 1907; abst. *J. S. C. I.* 1908, **27**, 749. E. P. 6265, 1908; abst. *J. S. C. I.* 1908, **27**, 501. D. R. P. 170585; abst. *Chem. Centr.* 1906, **77**, II, 184; *Chem. Ztg.* 1906, **30**, 588; *Chem. Zts.* 1907, **6**, 19; *Jahr. Chem.* 1905-1908, I, 1763, 1765; *Wag. Jahr.* 1906, **52**, I, 450; *Zts. ang. Chem.* 1907, **20**, 324. D. R. P. 179825; abst. *Chem. Zentr.* 1907, **78**, I, 915; *Chem. Ztg. Rep.* 1907, **30**, 84; *Jahr. Chem.* 1905-1908, I, 1765; *Wag. Jahr.* 1906, **52**, I, 451; *Zts. ang. Chem.* 1907, **20**, 1327. D. R. P. 179882; abst. *Mon. Sci.* 1909, **71**, 74; *Chem. Zentr.* 1907, **78**, I, 915; *Jahr. Chem.* 1905-1908, I, 1765; *Wag. Jahr.* 1907, **53**, I, 391; *Zts. ang. Chem.* 1907, **20**, 1327; *Zts. Schiess. Spreng.* 1907, **2**, 54. D. R. P. 188231; abst. *Chem. Zentr.* 1907, **78**, II, 1949; *Chem. Ztg. Rep.* 1907, **31**, 534; *Jahr. Chem.* 1905-1908, I, 1768; *Wag. Jahr.* 1908, **54**, I, 419; *Zts. ang. Chem.* 1908, **21**, 558. D. R. P. 214445; abst. *Chem. Zentr.* 1909, **80**, II, 1509; *Chem. Ztg. Rep.* 1909, **33**, 562; *Jahr. Chem.* 1909, **62**, I, 366; *Wag. Jahr.* 1909, **55**, I, 392; *Zts. ang. Chem.* 1909, **22**, 2337. D. R. P. 268828; abst. *C. A.* 1914, **8**, 2230; *Chem. Zentr.* 1914, **85**, I, 506; *Chem. Ztg. Rep.* 1914, **38**, 128; *Wag. Jahr.* 1914, **60**, I, 387; *Zts. ang. Chem.* 1914, **27**, 124. D. R. P. 284042; abst. *Chem. Zentr.* 1915, **86**, I, 1237; *Chem. Ztg. Rep.* 1915, **39**, 207; *Zts. ang. Chem.* 1915, **28**, 295. D. R. P. 287307; abst. *Chem. Ztg. Rep.* 1915, **39**, 387; *Zts. ang. Chem.* 1915, **28**, 530. U. S. P. 772862; abst. *J. S. C. I.* 1904, **23**, 1097; *Mon. Sci.* 1906, **65**, 337; *Chem. Zts.* 1905, **4**, 17. U. S. P. 775123; abst. *Mon. Sci.* 1906, **65**, 337. U. S. P. 802620, 837277, 889431. U. S. P. 906682; abst. *J. S. C. I.* 1909, **28**, 96; *Chem. Ztg.*

of the process and its many modifications is the subjection of the atmospheric gases to the electric arc of peculiar construction, formed between electrodes placed in a powerful magnetic field.

J. Plücker in 1861¹ showed how a disc of sparks is produced, when induction sparks from a large inductorium are caused to pass between electrodes, situated in the equatorial plane between the poles of a U-shaped electromagnet, similar discharges being experimented with later by D. Solomon,² W. Nernst,³ K. Jellinek⁴ and Lehmann.⁵

In the original process, in oxidizing gases by means of the electric arc, more especially for obtaining nitrogen oxides from

Rep. 1909, **33**, 53. U. S. P. 948158, 1011018. U. S. P. 1177359; abst. J. S. C. I. 1916, **35**, 539. U. S. P. 1200324; abst. J. S. C. I. 1916, **35**, 1233. U. S. P. 1236662; abst. J. S. C. I. 1917, **36**, 1047. Belg. P. 209895, 1908. F. P. 320498, 335692; abst. Mon. Sci. 1911, **75**, 571. F. P. 345969; abst. Mon. Sci. 1906, **65**, 54. F. P. 384870, 386059. F. P. 388276, 1908; abst. J. S. C. I. 1908, **27**, 897; Mon. Sci. 1909, **71**, 110; Chem. Ztg. Rep. 1908, **32**, 452. F. P. 442514, 465740; abst. C. A. 1914, **8**, 3492. Norw. P. 11445, 12879; abst. Mon. Sci. 1904, **61**, 125; Chem. Ztg. Rep. 1904, **28**, 531. Norw. P. 12989, 13035, 13040, 13052, 13240, 13244, 13279, 13280, 13281, 13705, 13738, 13753, 14229, 14350, 14585; abst. Mon. Sci. 1906, **65**, 177; Chem. Ztg. Rep. 1906, **30**, 21. Norw. P. 15052; abst. Chem. Ztg. Rep. 1906, **30**, 424. Norw. P. 15349, 15706; abst. Mon. Sci. 1907, **67**, 162; Chem. Ztg. Rep. 1906, **30**, 475. Norw. P. 15896, 15898, 16294, 17051; abst. Chem. Ztg. Rep. 1908, **32**, 65. Norw. P. 17287; abst. Mon. Sci. 1910, **73**, 34; Chem. Ztg. Rep. 1908, **32**, 160. Norw. P. 17400; abst. Mon. Sci. 1910, **73**, 39; Chem. Ztg. Rep. 1908, **32**, 201. Norw. P. 17429; abst. Mon. Sci. 1910, **73**, 39; Chem. Ztg. Rep. 1908, **32**, 201. Norw. P. 17499, 17557, 17558, 17559; abst. Chem. Ztg. Rep. 1908, **32**, 280. Norw. P. 17834, 17974, 17975, 18092, 18236, 18243, 18370, 18854; abst. Mon. Sci. 1912, **77**, 90; Chem. Ztg. Rep. 1909, **33**, 339. Norw. P. 19261, 19635; abst. Mon. Sci. 1913, **79**, 33; Chem. Ztg. Rep. 1910, **34**, 136. Norw. P. 20486, 20670; abst. C. A. 1912, **6**, 1887; Chem. Ztg. Rep. 1911, **35**, 137. Norw. P. 21334, 22631; abst. C. A. 1913, **7**, 541. Norw. P. 22894; abst. C. A. 1913, **7**, 2289; Chem. Ztg. Rep. 1913, **37**, 146. Norw. P. 23446, 23542; abst. C. A. 1914, **8**, 795; Chem. Ztg. Rep. 1913, **37**, 656. Norw. P. 24385, 24423; abst. Chem. Ztg. Rep. 1914, **38**, 499; Zts. ang. Chem. 1915, **28**, 206. Norw. P. 26329, 26865, 26882. Swiss P. 26130, 29711, 35950, 39061, 50256, 72824. Swed. P. 19987, 20095, 21089; abst. Chem. Ztg. Rep. 1906, **30**, 304. Swed. P. 21234, 23915, 24086, 25070, 28646, 30832, 38723, 40830, 40839; abst. C. A. 1916, **10**, 2620. India Appl. 26, 1904.

1. Pogg. Ann. 1861, **113**, 252; Bibl. Univ. Arch, 1862, **13**, 89.

2. Phil. Mag. 1896, (5), **42**, 258.

3. Zts. anorg. chem. 1906, **49**, 213; Zts. Elektrochem. 1906, **12**, 527; abst. J. C. S. 1906, **90**, ii, 437; J. S. C. I. 1906, **25**, 533; Bull. Soc. Chim. 1907, **2**, 414; Chem. Centr. 1906, **77**, II, 89; Jahr. Chem. 1905-1908, I, 1754; Wag. Jahr. 1906, **52**, I, 464; Zts. ang. Chem. 1907, **20**, 283.

4. Zts. anorg. Chem. 1906, **49**, 229; abst. J. C. S. 1906, **90**, ii, 437; J. S. C. I. 1906, **25**, 533; Chem. Centr. 1906, **77**, II, 89; Jahr. Chem. 1905-1908, I, 1755; Meyer Jahr. Chem. 1906, **16**, 35; Zts. ang. Chem. 1907, **20**, 283.

5. "Die elektr. Lichterscheinungen und Entladungen," 1898, 353.

atmospheric air, the arc is caused to spread out into more or less of a circular form, of about one meter in diameter, and the gas is passed through this extended arc. The spreading out of the arc is produced by forming the arc between the poles of an electromagnet. With currents of high voltage the poles are set a few millimeters from each other. When direct currents are used

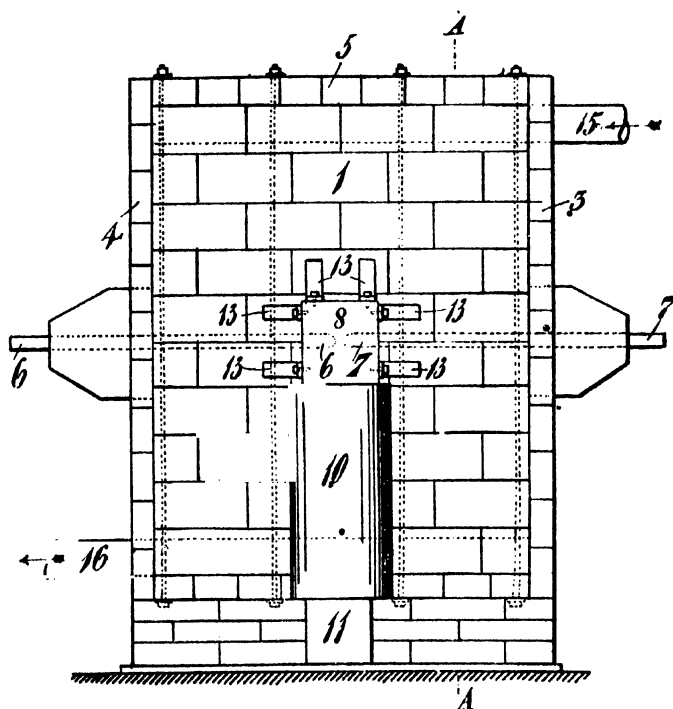


FIG. 77.—THE BIRKELAND-EYDE NITROGEN FIXATION FURNACE

several hundred arcs per second are formed. With alternating currents the currents are alternately above and below the conductors. The poles are provided with arrow-head projections of platinum. The arrangement of the furnace is shown in Figs. 77 and 78.

The principle upon which this process is based is that when

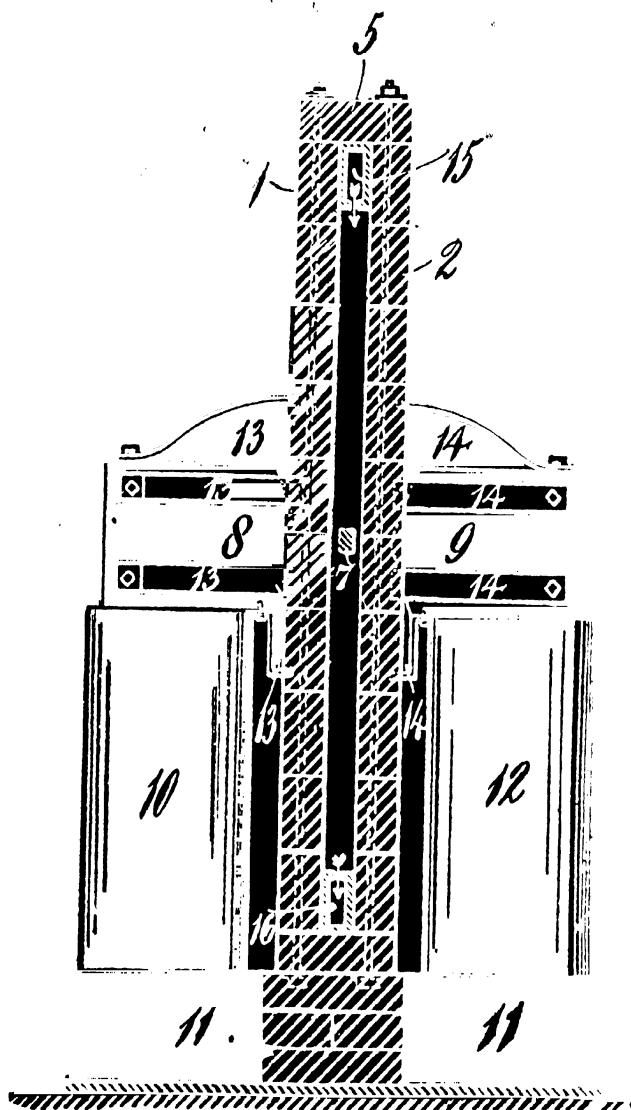


FIG. 78.—BIRKELAND-EYDE NITROGEN FIXATION FURNACE

an arc is formed between electrodes located in an electromagnetic field the power exerted by the latter forces the arc to leave the direct path between the terminal and to assume a curved form. The curve is pressed outward, its starting points retreating from the ends of both electrodes, until the length is such that the limit of resistance is reached. The arc, apparently, breaks and disappears, being simultaneously replaced by a new arc in a direct line between the electrodes. This arc undergoes the same cycle. This peculiar force developed in the electromagnetic field tends to extinguish the electric flame, and this phenomena has been termed the electromagnetic blast. The formation, expansion and extinction of an arc proceeds with great rapidity, often occurring as many as 1000 times per second. The rapidity is controlled in a measure by altering the power of the electromagnet, for practical purposes about 100 cycles per second having been found to produce the best results. The eye merely observes a thin continuous disc of flame at right angles to the line joining the poles of the electromagnet. As the arc in expanding moves more rapidly outward along the negative electrode than along the positive, the center of the flame must necessarily be diverted sidewise. If the electromagnet is fed by a direct current and a direct current passes through the electrodes, the flame assumes the form of a semicircle. When an alternating current serves the electromagnet and a direct current passing through the electrodes, arc expands in both directions, and a sheet of flame approximately circular in form is produced. The same result follows the use of an alternating current in the electrode and a direct current in the magnet.

The use of such an electric disc for effecting the combination of oxygen and nitrogen marked a decided advance in this art, and made it possible to inaugurate this industry on a satisfactory economic basis. Combined with great simplicity in mechanical detail, the relatively great surface and extreme tenuity of the electric disc rendered it possible to bring large volumes of air in contact with the intensely hot flame, and to cool the resultant products with great rapidity.

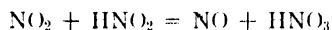
* According to T. Norton, while the economic value of the process depends largely on the outcome of the furnace reaction,

there is a secondary factor of considerable importance. This is the method used to isolate the nitric oxide from the large volume of gas issuing from the furnace and transforming it into nitric acid in a more or less dilute solution in water, or into some of the various nitrates or nitrites demanded by commerce. Chemically, the reaction in the furnace between the oxygen and the nitrogen of the air is represented by the equation $N_2 + O_2 = 2NO$. That is, one molecule of oxygen unites with one molecule of nitrogen to form two molecules of nitric oxide, a colorless gas. This nitric oxide unites readily with free oxygen, at temperatures below 620° to form nitrogen peroxide, a brown gas, with the formula NO_2 at temperatures above 140° , and the formula N_2O_4 , at low temperatures. The peroxide condenses at 22° to a liquid, which at -30° congeals to a mass of colorless crystals. As the temperature falls from 140° the number of molecules of N_2O_4 in a given volume steadily increases, as shown by the increase in density and the change in color from a deep brown to a reddish brown, and then to a yellowish brown. At 60° half of the molecules in the gas are of the formula N_2O_4 . At 28° they constitute 80%.

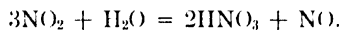
When the peroxide comes in contact with water it is dissolved and reacts, forming nitric acid and nitrous acid, thus:



With an excess of peroxide the nitrous acid is oxidized to nitric acid and oxide is liberated, as follows:



The net result of these two reactions is that two-thirds of the nitrogen peroxide is transformed into nitric acid according to the equation



The liberated nitric oxide, in the presence of oxygen and water, repeats the cycle of changes given above, so that theoretically it is possible to change to nitric acid all the nitric oxide in the current of gas issuing from the nitrate furnace.

The actual process of nitrogen peroxide production is not so simple as the equations indicate, and the plant required for the

purpose constitutes the most imposing feature of nitrate works. The gases leaving the furnace at a temperature of about 750° enter a huge main of iron lined with fire brick. Farther on the main is of aluminium, about 30 inches in diameter. This terminates at a large vat where the current of gas passes through a number of small tubes of aluminium, thus offering a large surface for cooling. Water can be heated in this vat or solutions can be evaporated. On leaving the vat the current is again concentrated in a single conduit, which leads to the steam chamber. Here the gas passes through tubular boilers and furnishes a large volume of steam, which can be used for evaporation or in the production of energy.

The gas possesses a temperature of about 200° on issuing from the boiler tubes. By passing through additional sets of aluminium cooling tubes the temperature is brought down to 50° C., and the current then enters two large chambers constructed of heavy iron plate, the walls being lined with material not affected by nitric acid. In these chambers the oxidation of the nitric oxide to nitrogen peroxide by means of the oxygen in the excess of air is completely effected. These chambers are of great capacity, so that the gases admitted remain in gentle movement for over a minute before reaching the outlet. This arrangement is rendered necessary by the fact that the oxidation requires some little time to be approximately complete. In a gaseous mixture containing 2% of nitric oxide, 50% of the latter is oxidized to peroxide in about 12 seconds, and 90% in not over 100 seconds time.

- The product of the furnace reaction, transformed into nitrogen peroxide, is now ready to undergo the final change into nitric acid. For this purpose the contents of the oxidation chambers are directed by powerful ventilators into enormous absorption towers. These are built of Norwegian granite, are 20 meters (65.62 feet) high and 5.5 meters (18 feet) in diameter. The great granite slabs are 25 centimeters in thickness and are held in place by strong iron bands. A cement composed of asbestos and water glass is employed for the joints. The interior is filled with fragments of quartz, and the top of the tower is provided with the usual devices for distributing a liquid in the interior. At the bottom is an outlet leading to a montejus of earthenware. Con-

nections are made principally by means of aluminium piping.

The systematic method of absorption is as follows: The current of gases is forced to pass through a series of three such towers, entering at the bottom and issuing at the top. In each tower it encounters a descending current of more or less dilute nitric acid, trickling downward over the quartz masses and offering a vast surface of liquid for the absorption of the nitric vapors. The acid in the first tower is near the point of maximum concentration, i. e., 50% HNO_3 (34.70° Baumé), that of the second is much more dilute, and that of the third tower is very dilute. The current of gases in its course encounters successively masses of liquid of increasingly greater absorptive powers, while its percentage of NO_2 is rapidly lowered. By the use of compressed air the acid solution is forced from the bottom of a tower to the distributing reservoir on the top of the same tower, or of its neighbor; or, if fully concentrated, it is directed into large reservoirs of granite.

The contents of the first tower are passed repeatedly over the quartz filling until this maximum concentration is attained. Then either all or a part of the liquid is transferred to a storage reservoir and is replaced by a corresponding quantity from the second tower. A similar amount is contributed to the latter from a third tower, and in its place comes a supply of fresh water. In the second and third towers the solution is also forced to pass several times from top to bottom before the required strength is obtained. The cycle of reactions above enumerated is uninterruptedly in operation at all points in the series of towers. The practical result is that nitric acid, of 50% strength and free from nitrous acid, is continually withdrawn from the base of the first tower. In the other towers the solutions in movement contain increasingly large proportions of nitrous acid. An exceedingly ingenious automatic device is attached to each tower, controlling the action of the pumps and the movements of the absorbent solution. As in the furnace room, there is need of only a limited number of operatives in the group of towers.

As the percentage of peroxide in the air current decreases, the rate of absorption becomes more and more sluggish. When the air current issues from the third tower it still contains a

certain amount of unabsorbed peroxide sometimes as high as 20% of the original quantity. In order to save as much as possible of this fraction the stream of gas is passed through another large absorption tower built of wood and lined with brick in which water is replaced by a solution of sodium carbonate or by milk of lime. The rate of absorption is much more rapid here, and a mixed solution of nitrate and nitrite is obtained. From this last tower the current of gases is conducted through a chamber filled with fragments of quicklime, and finally issues into the air. It still contains from 2% to 2.5% of the combined nitrogen yielded by the electric furnace and at present this is lost. The mixed solution of nitrate and nitrite when sufficiently concentrated, can be evaporated and used directly for fertilizing or it can be changed into nitrate by treatment with an adequate amount of nitric acid, the liberated nitrous vapors being directed into the absorption towers. Various modifications in the disposition and use of the final absorption in alkaline solutions will be noted later. A multitude of minor details, such as the clever automatic device for regulating the movement of liquids in the absorption tower, the use of aluminium connections, etc., all testify to the intelligent manner in which the Norwegian engineers have overcome the manifold technical difficulties in the way of transforming the nitric oxide supplied by the furnaces into the nitric acid and nitrates.

The absorption towers yield chiefly 50% nitric acid and secondarily calcium nitrate or other alkaline nitrates, as desired. The commercial products thus brought upon the market by the Notodden works are nitric acid in varying degrees of concentration, calcium nitrate, sodium nitrite, ammonium nitrate, and such small amounts of other nitrates as the local industries in Norway require. Concentrated nitric acid is manufactured to some extent at Notodden by evaporation of the 50% acid secured from the towers. The steam secured in cooling the hot gas current is used for the purpose of heating the distillation vessels. On account of the difficulties attending the transportation of this acid, no attempt is made to give it prominence in the general scheme of manufacture, or to do more than supply a purely local demand.

Figs. 79, 80 and 81 show diagrammatically, in section and

2. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, D. R. P. 284042;

absorbed in the quicklime at 300° – 400° .¹ Or,² the gases are concentrated by absorption in alkalis, and decomposing the alkaline compound by heating with alkaline earth or other metallic oxides or silicon, the nitrogen oxides thus obtained being then

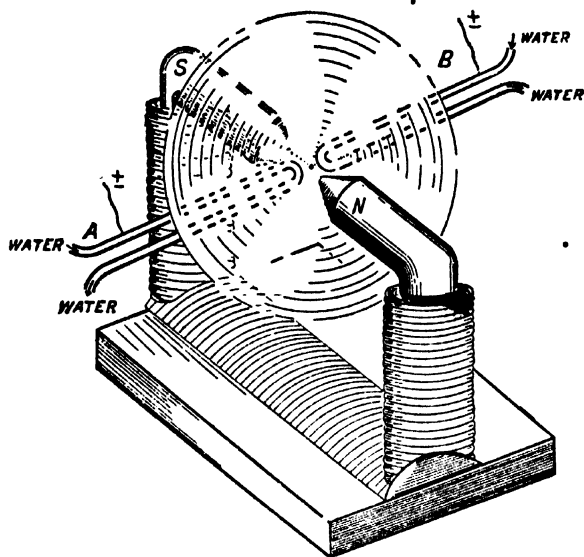


FIG. 80.—BIRKELAND-EYDE ELECTRIC FURNACE (DIAGRAMMATIC)

oxidized to nitric acid. By a modification in procedure,³ nitrites may be obtained instead of nitrate. To the above calcium nitrate may be added⁴ when by double decomposition ammonium nitrate is formed and may be recovered by evaporation to crystal-

abst. Chem. Zentr. 1915, **86**, I, 1237; Chem. Ztg. Rep. 1915, **39**, 207; Zts. ang. Chem. 1915, **28**, 295. D. R. P. 287307; abst. Chem. Ztg. Rep. 1915, **39**, 387; Zts. ang. Chem. 1915, **28**, 530. F. P. 465740; abst. C. A. 1914, **8**, 3492. F. P. 492379, 1919; abst. Chim. Ind. 1920, **3**, 212. Norw. P. 26882.

1. A. Schloesing, F. P. 460328, Chem. Ztg. Rep. 1914, **38**, 430. U. S. P. 1177359; abst. J. S. C. I. 1914, **33**, 23; 1916, **35**, 539.

2. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, Swed. P. 40839, 1916; abst. C. A. 1916, **10**, 2620.

3. De Norske Saltpeterværker, Norw. P. 22631, 1910; abst. C. A. 1913, **7**, 541; Chem. Ztg. Rep. 1912, **36**, 628.

4. K. Birkeland, E. P. 25632, 1907; J. S. C. I. 1908, **27**, 749.

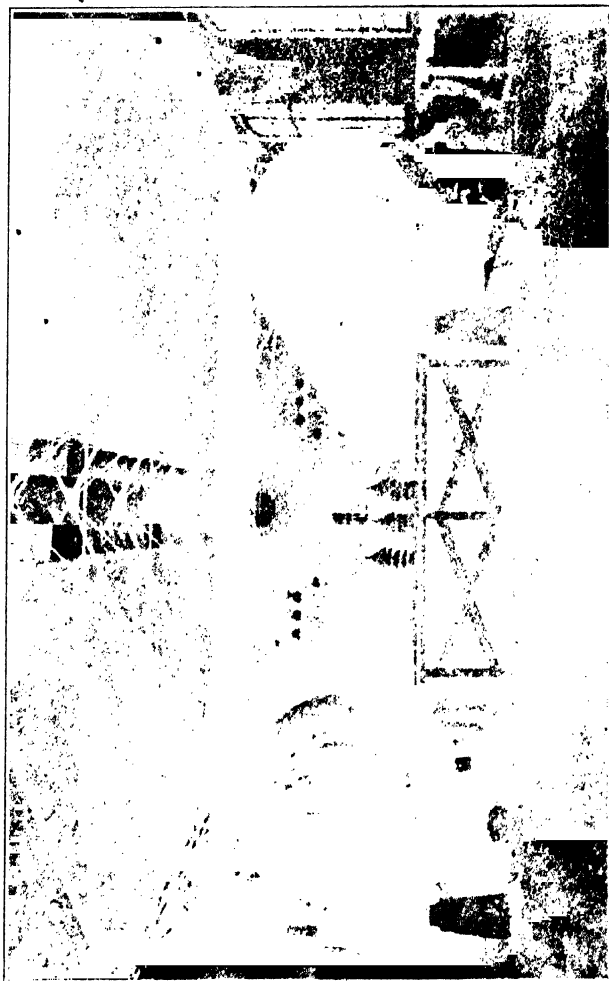


FIG. 81.—BIRKELAND-EYDE FURNACES (BJUKAN SALTPETER FACTORY).

lization, when a satisfactory yield is obtained.

In a more recent process,¹ the oxidation and absorption of the nitrogen and oxygen may be effected in a closed system in which the gases are circulated under pressure. The circulating gases are maintained at their original volume and pressure by supplying a compressed gas mixture of suitable composition and quantity, at a certain point. To prevent accumulation of impurities, a portion of the residual gases leaving the absorption system may be withdrawn previous to the introduction of fresh compressed gas. The gas withdrawn is relatively rich in argon, etc., and may be utilized for the manufacture of argon. The gaseous mixture most favorable to the reaction is $O_2:N_2 = 1:1$.

Pauling Processes for Nitric Acid Manufacture. H. and G. Pauling and the Saltpetersaure Industrie Gesellschaft, to whom many of the patents have been assigned,² have approached the

1. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, E. P. 190099, 1916; abst. J. S. C. I. 1917, **36**, 214; C. A. 1916, **10**, 2621.

2. For résumé of the Pauling patents, consult U. S. P. 739920, 739921; abst. J. S. C. I. 1903, **22**, 1135. U. S. P. 758774; abst. J. S. C. I. 1904, **23**, 545; Mon. Sci. 1904, **61**, 125; Chem. Zts. 1904, **3**, 648. U. S. P. 758775, 777485. U. S. P. 777486; abst. Mon. Sci. 1905, **63**, 116. U. S. P. 807491; 1905; abst. Zts. ang. Chem. 1906, **19**, 1104; J. S. C. I. 1903, **22**, 1135; Mon. Sci. 1906, **65**, 96; Chem. Zts. 1906, **5**, 87. U. S. P. 814917, 1906; abst. Proc. Roy. Soc. **13**, 280; Mon. Sci. 1906, **65**, 115. U. S. P. 873891, 1906; abst. J. S. C. I. 1906, **25**, 928; Mon. Sci. 1908, **69**, 50. U. S. P. 877446, 1908; abst. J. S. C. I. 1908, **27**, 160; Mon. Sci. 1908, **69**, 57; Chem. Ztg. Rep. 1908, **32**, 129. U. S. P. 877447, 1908; abst. J. S. C. I. 1908, **27**, 160; Mon. Sci. 1908, **69**, 57; Chem. Ztg. Rep. 1908, **32**, 108. U. S. P. 882958, 1908; abst. Mon. Sci. 1909, **71**, 28. U. S. P. 887266, 1906; abst. J. S. C. I. 1907, **26**, 24; Mon. Sci. 1909, **71**, 113. U. S. P. 896144; abst. Mon. Sci. 1909, **71**, 125; Chem. Ztg. Rep. 1908, **32**, 510. U. S. P. 898133, 1907; abst. J. S. C. I. 1907, **26**, 1243; Chem. Ztg. Rep. 1908, **32**, 572. U. S. P. 991356, 1911; abst. J. S. C. I. 1910, **29**, 1157; Mon. Sci. 1912, **77**, 17. U. S. P. 991357, 1910; abst. J. S. C. I. 1911, **30**, 360; Mon. Sci. 1912, **77**, 17. U. S. P. 993868, 1911; abst. J. S. C. I. 1911, **30**, 541; Mon. Sci. 1912, **77**, 18; Chem. Ztg. Rep. 1911, **35**, 342. U. S. P. 999587, 1911; abst. J. S. C. I. 1911, **30**, 1071; Mon. Sci. 1912, **77**, 25. U. S. P. 1029885, 1912; abst. J. S. C. I. 1912, **31**, 691; C. A. 1912, **6**, 2362; Mon. Sci. 1913, **79**, 11. U. S. P. 1031864, 1912; abst. J. S. C. I. 1912, **31**, 775; C. A. 1912, **6**, 2676. U. S. P. 1031865, 1912; abst. J. S. C. I. 1912, **31**, 775; C. A. 1912, **6**, 2676; Mon. Sci. 1913, **79**, 3. U. S. P. 1037977, 1912; abst. J. S. C. I. 1912, **31**, 923; C. A. 1912, **6**, 3308. U. S. P. 1074287, 1913; abst. J. S. C. I. 1913, **32**, 1009; C. A. 1913, **7**, 3821. U. S. P. 1079541; abst. C. A. 1914, **8**, 405; Mon. Sci. 1914, **81**, 27. E. P. 18427, 1902; abst. J. S. C. I. 1903, **22**, 795. E. P. 21828, 1902; abst. J. S. C. I. 1903, **22**, 795; Chem. Ztg. 1904, **28**, 157. E. P. 5540, 1901; abst. J. S. C. I. 1905, **24**, 276. E. P. 7869, 1906; abst. J. S. C. I. 1906, **25**, 935; Zts. Elektrochem. 1907, **13**, 228. E. P. 7870, 1906; abst. J. S. C. I. 1906, **25**, 758. E. P. 7871, 1906; abst. J. S. C. I. 1906, **25**, 758. E. P. 8152, 1906; abst. J. S. C. I. 1906, **25**,

problem from a somewhat different angle, they producing a large sheet of flame electrically by the use of divergent rather than

1052. E. P. 18435, 1906; F. P. 368715; abst. J. S. C. I. 1907, **26**, 23; 829; Zts. Elektrochem. 1907, **13**, 226. E. P. 18599, 1906; abst. J. S. C. I. 1907, **26**, 23; Zts. Elektrochem. 1907, **13**, 280. E. P. 18600, 1906; F. P. 371883; abst. J. S. C. I. 1907, **26**, 417; Zts. Elektrochem. 1907, **13**, 280. E. P. 18603, 1906; F. P. 368716; abst. J. S. C. I. 1907, **26**, 24, 157, 971. D. R. P. 180052, 1905; Mon. Sci. 1909, **71**, 74; Chem. Zentr. 1907, **78**, I, 1083; Chem. Ztg. Rep. 1907, **31**, 86; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1906, **52**, I, 446; Zts. ang. Chem. 1907, **20**, 1329; Zts. Schiess. Spreng. 1907, **2**, 35. Swiss. P. 37900, 1906; Aust. P. 28680, 1907. E. P. 7320, 1907; F. P. 375268; abst. J. S. C. I. 1907, **26**, 930, 1204. E. P. 18900, 1907; abst. J. S. C. I. 1907, **26**, 1204. E. P. 18901, 1907; abst. J. S. C. I. 1907, **26**, 1243. E. P. 23385, 1908; abst. J. S. C. I. 1910, **29**, 88. E. P. 27473, 1908; abst. J. S. C. I. 1909, **28**, 465. E. P. 6429, 1909; abst. J. S. C. I. 1909, **28**, 943. E. P. 8443, 1909; abst. J. S. C. I. 1909, **28**, 715. E. P. 19466, 1909; D. R. P. 216090; abst. J. S. C. I. 1910, **29**, 221; 1909, **28**, 1317. E. P. 22037, 1909; abst. J. S. C. I. 1910, **29**, 211; C. A. 1910, **4**, 2555; Chem. Ztg. Rep. 1911, **35**, 54. E. P. 9884, 1910; abst. J. S. C. I. 1910, **29**, 1157. E. P. 22319, 1910; F. P. 420252; abst. J. S. C. I. 1911, **30**, 360, 685. E. P. 22320, 1910; abst. J. S. C. I. 1911, **30**, 84; Chem. Ztg. Rep. 1911, **35**, 66. E. P. 22322, 1910; abst. J. S. C. I. 1911, **30**, 84. E. P. 3251, 1911; abst. J. S. C. I. 1911, **30**, 905. E. P. 8533, 1911; F. P. 422902; abst. J. S. C. I. 1911, **30**, 541; 1912, **31**, 231; C. A. 1912, **6**, 2825. E. P. 14121, 1911; abst. J. S. C. I. 1911, **30**, 1252; C. A. 1913, **7**, 221. E. P. 14122, 1911; abst. J. S. C. I. 1911, **30**, 1252; C. A. 1913, **7**, 221. E. P. 21478, 1912; U. S. P. 1029886; abst. J. S. C. I. 1912, **31**, 691; 1913, **32**, 296; C. A. 1914, **8**, 872. E. P. 18113, 1913; abst. J. S. C. I. 1914, **33**, 790. F. P. 323760, 1902; abst. J. S. C. I. 1903, **22**, 495; Mon. Sci. 1906, **65**, 336; 1911, **75**, 571, 572. F. P. 325244, 1904; abst. J. S. C. I. 1904, **23**, 515; Mon. Sci. 1901, **61**, 44; 1906, **65**, 336. F. P. 365070, 1906; abst. J. S. C. I. 1906, **25**, 928; Mon. Sci. 1907, **67**, 94; 1911, **75**, 571. F. P. 368715, 1906; abst. J. S. C. I. 1907, **26**, 23; Mon. Sci. 1911, **75**, 571. E. P. 368716, 1906; abst. J. S. C. I. 1907, **26**, 24. F. P. 368717, 1906; abst. J. S. C. I. 1907, **26**, 23; Zts. Elektrochem. 1907, **13**, 280; Mon. Sci. 1911, **75**, 571, 572. F. P. 371883, 1906; abst. J. S. C. I. 1907, **26**, 417; Mon. Sci. 1911, **75**, 573. F. P. 374237; abst. Mon. Sci. 1908, **69**, 139; Chem. Ztg. Rep. 1907, **31**, 309. 10023, addn. to 334237. F. P. 374238, 1906; abst. J. S. C. I. 1907, **26**, 766. F. P. 374278, 1906; abst. J. S. C. I. 1906, **25**, 935; Zts. Elektrochem. 1907, **13**, 228. F. P. 374327, 1908; 375268, 1907; abst. J. S. C. I. 1907, **26**, 930. F. P. 380059, 1907; abst. J. S. C. I. 1907, **26**, 1204; Mon. Sci. 1909, **71**, 99; Chem. Ztg. Rep. 1908, **32**, 178. F. P. 380060, 1907; abst. J. S. C. I. 1907, **26**, 1243. F. P. 397666, 400745; abst. J. S. C. I. 1909, **28**, 943. F. P. 400771, 1909; abst. J. S. C. I. 1909, **28**, 715. F. P. 406442, 1908; abst. J. S. C. I. 1909, **28**, 1317; Mon. Sci. 1911, **75**, 571, 572. F. P. 407133, 1909; abst. J. S. C. I. 1910, **29**, 565; Mon. Sci. 1910, **73**, 175; Chem. Ztg. Rep. 1910, **34**, 187. F. P. 415749, abst. J. S. C. I. 1910, **29**, 1157; Mon. Sci. 1913, **79**, 82; C. A. 1912, **6**, 1966; Chem. Ztg. Rep. 1910, **34**, 561. F. P. 420252, abst. J. S. C. I. 1911, **30**, 360; C. A. 1912, **6**, 1967; Mon. Sci. 1911, **75**, 572; 1913, **79**, 88; Chem. Ztg. Rep. 1911, **35**, 303. F. P. 420803, 1910; abst. J. S. C. I. 1911, **30**, 84; Mon. Sci. 1913, **79**, 113. F. P. 420804, 1910; abst. J. S. C. I. 1911, **30**, 84. F. P. 422902, 1911; abst. J. S. C. I. 1911, **30**, 541. F. P. 425765, 1911. F. P. 430111, 1911; abst. J. S. C. I. 1912, **31**, 138. F. P. 430112, 1911; abst. J. S. C. I. 1912, **31**, 138; Mon. Sci. 1913, **79**, 127. F. P. 430113, 1911; abst. J. S. C. I. 1911, **30**, 1252. F. P. 450448, abst. C. A. 1913, **7**, 2999; Chem. Ztg. Rep. 1913, **37**, 281. F. P. 461326, abst. J. S. C. I. 1913, **32**, 1009. F. P. 463859, abst. C. A. 1914, **8**, 2927; Chem. Ztg. Rep. 1914,

convergent electrodes, assisted by a powerful air blast at the point of divergence. This method has been operating success-

- 33**, 310. U. S. P. 807491, 1905; abst. Zts. ang. Chem. **19**, 1104. D. R. P. 152805, 1901; abst. Zts. ang. Chem. 1904, **17**, 1768; Chem. Zentr. 1904, **75**, II, 486; Chem. Ztg. Rep. 1904, **28**, 707; Chem. Zts. 1905, **4**, 51; Wag. Jahr. 1904, **50**, I, 340. D. R. P. 180691, 1905; abst. Zts. ang. Chem. 1907, **20**, 1328; Chem. Zentr. 1907, **78**, I, 1519; Chem. Ztg. Rep. 1907, **31**, 115; Chem. Zts. 1907, **6**, 75; Jahr. Chem. 1905-1908, I, 1766; Wag. Jahr. 1907, **53**, I, 386. D. R. P. 182849; abst. Mon. Sci. 1911, **75**, 15; Chem. Zentr. 1907, **78**, II, 651; Chem. Ztg. Rep. 1907, **31**, 168; Jahr. Chem. 1905-1908, I, 1766; Wag. Jahr. 1907, **53**, I, 482; Zts. ang. Chem. 1907, **20**, 800. D. R. P. 184958, 1904; abst. Zts. ang. Chem. 1908, **21**, 558; Mon. Sci. 1909, **71**, 160; Chem. Zentr. 1907, **78**, II, 1136; Jahr. Chem. 1905-1908, I, 1767; Wag. Jahr. 1907, **53**, I, 387. D. R. P. 186454, 1906; abst. Zts. ang. Chem. 1908, **21**, 558; Chem. Zentr. 1907, **78**, II, 1130; Chem. Ztg. Rep. 1907, **31**, 351; Jahr. Chem. 1905-1908, I, 1767; Wag. Jahr. 1907, **53**, I, 388; Zts. Schiess. Spreng. 1907, **2**, 354. D. R. P. 187367; abst. C. A. 1908, **2**, 576; Chem. Zentr. 1907, **78**, II, 1281; Chem. Ztg. Rep. 1907, **31**, 454; Chem. Zts. 1907, **6**, No. 188; Jahr. Chem. 1905-1908, I, 1768; Wag. Jahr. 1907, **53**, I, 388; Zts. ang. Chem. 1908, **21**, 558. D. R. P. 193402, 1907; abst. Zts. ang. Chem. 1908, **21**, 412; Chem. Zentr. 1908, **79**, I, 316; Chem. Ztg. Rep. 1908, **32**, 41; Jahr. Chem. 1905-1908, I, 1769; Wag. Jahr. 1907, **53**, I, 408. D. R. P. 193366, abst. Chem. Zentr. 1908, **79**, I, 905; Chem. Ztg. Rep. 1908, **32**, 108; Chem. Zts. 1908, **7**, 638; Wag. Jahr. 1907, **53**, I, 389; Zts. ang. Chem. 1908, **21**, 556. D. R. P. 196112; abst. Chem. Zentr. 1908, **79**, I, 1220; Mon. Sci. 1911, **75**, 58; Chem. Zts. 1908, **7**, 719; Jahr. Chem. 1905-1908, I, 1797; 1909, **62**, I, 534; Wag. Jahr. 1908, **54**, I, 424; Zts. ang. Chem. 1908, **21**, 1084; Zts. Schiess. Spreng. 1908, **3**, 194. D. R. P. 198241; abst. Chem. Zentr. 1908, **79**, I, 1863; Chem. Ztg. Rep. 1908, **32**, 277; Jahr. Chem. 1905-1908, I, 1771; Wag. Jahr. 1908, **54**, I, 413; Zts. ang. Chem. 1908, **21**, 1562. D. R. P. 202763; abst. Chem. Zentr. 1908, **79**, II, 1651; Chem. Ztg. Rep. 1908, **32**, 623; Jahr. Chem. 1905-1908, I, 1773; Wag. Jahr. 1908, **54**, I, 413; Zts. ang. Chem. 1908, **21**, 2472. D. R. P. 203747; abst. Chem. Zentr. 1908, **79**, II, 1652; Chem. Ztg. Rep. 1908, **32**, 623; Chem. Zts. 1909, **8**, 1281; Jahr. Chem. 1905-1908, I, 1773; Wag. Jahr. 1908, **54**, I, 414; Zts. ang. Chem. 1908, **21**, 2518. D. R. P. 205018, addn. to D. R. P. 196112; abst. Mon. Sci. 1912, **77**, 50; Chem. Zentr. 1909, **80**, I, 324; Chem. Ztg. Rep. 1909, **33**, 7; Jahr. Chem. 1909, **62**, 534; Wag. Jahr. 1908, **54**, I, 424; Zts. ang. Chem. 1909, **22**, 208. D. R. P. 205464; abst. Chem. Zentr. 1909, **80**, I, 803; Chem. Ztg. Rep. 1909, **33**, 53; Wag. Jahr. 1908, **54**, II, 394; Zts. ang. Chem. 1909, **22**, 498. D. R. P. 211919; abst. Mon. Sci. 1912, **77**, 99; Chem. Zentr. 1909, **80**, II, 944; Chem. Ztg. Rep. 1909, **33**, 420; Jahr. Chem. 1909, **62**, I, 373; Wag. Jahr. 1909, **55**, I, 604; Zts. ang. Chem. 1909, **22**, 1724. D. R. P. 213710; abst. Chem. Zentr. 1909, **80**, II, 1392; Chem. Ztg. Rep. 1909, **33**, 531; Wag. Jahr. 1909, **55**, I, 390; Zts. ang. Chem. 1909, **22**, 2244. D. R. P. 216090, 1908; abst. J. S. C. I. 1909, **28**, 1317; 1910, **29**, 221; Chem. Zentr. 1909, **80**, II, 2053; Chem. Ztg. Rep. 1909, **33**, 666; Wag. Jahr. 1909, **55**, I, 398; Zts. ang. Chem. 1910, **23**, 90. D. R. P. 231584; abst. Chem. Zentr. 1911, **82**, I, 767; Chem. Ztg. Rep. 1911, **35**, 162; Wag. Jahr. 1911, **57**, I, 462; Zts. ang. Chem. 1911, **24**, 563. D. R. P. 235299; abst. C. A. 1911, **5**, 3136; Chem. Zentr. 1911, **82**, II, 111; Chem. Ztg. Rep. 1911, **35**, 342; Wag. Jahr. 1911, **57**, I, 464; Zts. ang. Chem. 1911, **24**, 1444. D. R. P. 237684; abst. C. A. 1912, **6**, 1508; Chem. Zentr. 1911, **82**, II, 812; Chem. Ztg. Rep. 1911, **35**, 464; Wag. Jahr. 1911, **57**, I, 472; Zts. ang. Chem. 1911, **24**, 1882; Zts. Schiess. Spreng. 1911, **6**, 411. D. R. P. 241882; abst. C. A. 1912, **6**, 2039; Chem. Zentr. 1912, **83**, I, 171; Chem. Ztg. Rep. 1912, **36**, 43; Wag. Jahr.

fully on a manufacturing scale since 1910. They spread¹ the arc-discharges used in the electric treatment of gases for the production of nitric acid from air, the gas to be treated being supplied from blast pipes placed at or near the point of greatest proximity of the diverging electrodes.

In the earlier development of this process Pauling made use of a cone of electric flame, the electrodes being hollow and located in a cylindrical chamber, one being pointed, and through which a blast of air entered the furnace. The second electrode, which was placed opposite, terminated in a large saucer-shaped surface, which was perforated with many small openings to allow the gas to pass out. By means of an air current the arc was lengthened as in the Schönherr methods. In a subsequent patent a fixed bar as one electrode was employed. The entering air is raised

1911, **57**, I, 637; Zts. ang. Chem. 1912, **25**, 135. D. R. P. 244840; abst. Chem. Zentr. 1911, **83**, I, 1162; Chem. Ztg. Rep. 1912, **36**, 234; Wag. Jahr. 1912, **58**, I, 419; Zts. ang. Chem. 1912, **25**, 858; Zts. Schiess. Spreng. 1912, **7**, 226. D. R. P. 246712; abst. C. A. 1912, **6**, 2504; Chem. Zentr. 1912, **83**, I, 1872; Chem. Ztg. Rep. 1912, **36**, 302; Wag. Jahr. 1912, **58**, I, 420; Zts. ang. Chem. 1912, **25**, 1648; Zts. Schiess. Spreng. 1912, **7**, 248. D. R. P. 250968; abst. Chem. Zentr. 1912, **83**, II, 1586; Chem. Ztg. Rep. 1912, **36**, 618; Wag. Jahr. 1912, **58**, I, 413; Zts. ang. Chem. 1912, **25**, 2377. D. R. P. 257809; abst. C. A. 1913, **7**, 2458; Chem. Zentr. 1913, **84**, I, 1245; Chem. Ztg. Rep. 1913, **37**, 166; Wag. Jahr. 1913, **59**, I, 434; Zts. ang. Chem. 1913, **26**, 235; Zts. Schiess. Spreng. 1913, **8**, 178. D. R. P. 258385; abst. C. A. 1913, **7**, 2517; Chem. Zentr. 1913, **84**, I, 1478; Chem. Ztg. Rep. 1913, **37**, 225; Wag. Jahr. 1913, **59**, I, 519. D. R. P. 259815; abst. C. A. 1913, **7**, 3084; Chem. Zentr. 1913, **84**, I, 2009; Chem. Ztg. Rep. 1913, **37**, 320; Wag. Jahr. 1913, **59**, I, 519; Zts. ang. Chem. 1913, **26**, 346. D. R. P. 268410; abst. C. A. 1914, **8**, 1654; Chem. Zentr. 1914, **85**, I, 306; Chem. Ztg. Rep. 1914, **38**, 37; Wag. Jahr. 1913, **59**, I, 525; Zts. ang. Chem. 1914, **27**, 49. D. R. P. 269238; abst. C. A. 1914, **8**, 1921; Chem. Zentr. 1914, **85**, I, 587; Chem. Ztg. Rep. 1914, **38**, 63; Wag. Jahr. 1914, **60**, I, 352; Zts. ang. Chem. 1914, **27**, 126. D. R. P. 274165, 1912; addn. to D. R. P. 257809; abst. C. A. 1914, **8**, 2939; Chem. Zentr. 1914, **85**, I, 1981; Chem. Ztg. Rep. 1914, **38**, 323; Wag. Jahr. 1914, **60**, I, 355; Zts. ang. Chem. 1914, **27**, 397. D. R. Ann. A. 26008, 26009, 30577, 31188, 31189, 31716. Aust. P. 27726, 33087, 33485, 33486, 34029, 40840. Aust. P. 40843, 1909; addn. to Aust. P. 33087. Aust. P. 48815, 48816; abst. Zts. Schiess. Spreng. 1911, **6**, 377. Aust. P. 49035, 52441, 53291, 1912, 61387. Swiss. P. 27533; abst. Chem. Zts. 1904, **3**, 372. Swiss. P. 37037, 42511, 1907; 53214, 1910; 53215, 53779, 55034, 56245, 56360, 57531, 65916. Swed. P. 16099, 23258, 28333; addn. to Swed. P. 23258; 32202, 38962. See also Zts. Elektrochem. 1907, **13**, 225, 284; 1909, **15**, 544; 1911, **17**, 431. Nor. P. 12416, 12721, 15970, 16035, 16368, 17170, 17286, 17402, 18237, 19345, 20113, 20360, 20408, 20693, 21153, 21362, 21760, 22369, 23163, 23164, 23335, 24238, 26479. Belg. P. 165133, 166525, 1902; 229235, 1910; 259112, 1913. Chem. Ztg. Rept. 1907, **31**, 454; 1908, **32**, 41, 108, 245, 277, 623; 1909, **33**, 531, 666; 1911, **35**, 312; 1912, **36**, 43; 1913, **37**, 225.

1. E. P. 18599, 1906; abst. J. S. C. I. 1907, **26**, 23.

above 1000° ,¹ and the gases then suddenly cooled.² The electrodes are made of oxidizable metals such as iron, so that when the arc is passing between the electrodes, a layer of melted oxide is produced and maintained thereon.³

Air is forced into the furnace through a number of small openings in a pipe situated on one side between the electrodes. When in operation the arc continually changes its position from one end to the other of the fixed electrodes, thus permitting rapid fluctuations of temperature in the air current. It was in 1906 that the Pauling's patented the process now in use, the rights to which have been acquired by the Saltpetersaure Industrie Ges. He then produced the arc between main electrodes at a considerable distance apart by blowing on to them, by means of a current of gas, the discharges which pass between supplementary electrodes at a short distance apart. His first patent issued in 1902, described the preparation of nitrogen peroxide and nitric acid by heating a mixture of air and steam, or air and oxyhydrogen gas until the water or gas becomes disassociated. The process was actually carried out by passing the mixture through a white hot, thin-walled porous porcelain tube. The reddish brown vapor passing out of the end of the tube was collected and converted by oxidation into nitric acid. The hydrogen, which diffused through the walls of the tubes, may be collected or caused to combine with another body such as chlorine to form HCl.⁵

In placing these patented processes upon an economic basis, an experimental plant was erected at Gelsenkirchen, which was succeeded in 1909 by a large permanent plant near Innsbruck in the Austrian Tyrol. In the Pauling furnace, curved electrodes are so located that the lower portions are in close proximity, while the upper portions are inclined at an angle of about 90° to each other. Narrow so-called "kindling blades" pass through slits in the curves. By means of the handles, connected by the isolators, these blades can be adjusted separately and very accurately, so as to present at one point a very short distance for the passage of the electric arc. A pipe situated immediately below this point

1. E. P. 18427, 1902; abst. J. S. C. I. 1903, **22**, 795.
2. E. P. 5540, 1904; abst. J. S. C. I. 1905, **24**, 276.
3. E. P. 18600, 1906; abst. J. S. C. I. 1907, **26**, 971.
4. E. P. 7869, 1906; abst. J. S. C. I. 1906, **25**, 935.
5. E. P. 21828, 1902; abst. J. S. C. I. 1903, **22**, 795.

admits of the entrance of an air blast. Its nozzle is so constructed that the air current issues well spread out somewhat in the shape of a fan, and fills the space between the inclined electrodes.

When an alternating current is passed through the circuit¹ an arc is formed between the nearest points of the two electrodes, viz., between the extremities of the narrow adjustable blades. Under the pressure of the air blast it is forced upward, fills the space between the electrodes, and projects far above them, attaining ordinarily a total height of 25 to 30 inches. To the eye, there is a continuous flame. Actually, with the rapid alternations of the current, the flame forms, only to vanish almost instantaneously and to reappear as quickly, being rekindled at the lowest point, where the terminals are nearest one another. The action of the sheet of flame is the same as in the other processes already described. The chief merit of the Pauling method lies in the very simple but practical provision for rekindling the arc at each half period of the electric current. The problem involves two leading factors. The distance between the electrodes at their nearest point must be sufficient to allow the easy passage between them of the powerful blast of air, without any material interference in the latter's direction, as influenced by the construction of the nozzle. This distance is ordinarily 40 millimeters (1.5748 inches). Such an interval demands, however, an electric current of exceptionally high tension in order to kindle the arc, especially when the rapid stream of air is passing through it. Once in activity, the arc is maintained with the aid of a current of low tension. It is here that the "kindling blades" come into play. They are so narrow that they offer practically no obstruction to the blast of air passing the bulky electrodes. They are adjusted so that their extremities almost touch. (The actual distance is 2 to 3 millimeters.) An electric current of low tension can thus be used to rekindle and maintain the sheet of flame. Once kindled between the points of the blades, it instantaneously fills the fan-shaped space between the main electrodes.

The electrodes are made of cast steel and are kept cool by the circulation of a current of water. They last for about 200

1. Data in connection with the above description of the Pauling process has been obtained from "Utilization of Atmospheric Nitrogen," T. Norton, 1912, pp. 66-68.

hours. The "kindling blades" are naturally more rapidly corroded, and it is necessary to adjust them at frequent intervals so as to insure the proper distance between their points. They last about 20 hours, but are easily replaced. The easy adjustment of the blades, combined with the permanent location of the electrodes, are all-important features. The resultant flame presents to the eye the appearance of uniform size and intensity.

The Pauling system includes another valuable feature in connection with the cooling of the current of air which has passed through the flame. A portion of the current, which after issuing from the furnace has been cooled down to the proper temperature to enter the peroxide chambers, is switched off before reaching the latter and blown into the upper parts of the flame from nozzles placed at its edges. The pressure of this cooling current is less than that under which the main air stream enters between the electrodes. As a result the gases in the upper zones of the flame are rapidly chilled to a much lower temperature, and the secondary current exerts a certain suction, which broadens and heightens the sheet of flame. The gas stream leaving the furnace contains 1.15% to 1.5% of nitric oxide.

As in the other processes already described, the Pauling electric flame operates inside a furnace of refractory material. It has been found that the best results are secured by employing two arc flames in a single furnace.

The type of furnace now in actual use requires a current of 400 kilowatts for each unit in operation, with an electromotive force of 4000 volts. A volume of 21,200 cubic feet of air is blown into a furnace in the course of an hour. One operative attends to 6 furnaces, and the factory of the company now includes 24 furnaces. One peculiar feature connected with the transmission of the current of the Pauling furnaces deserves notice. By its aid a number of furnaces can be introduced into a single circuit. As stated above, two arcs are employed in each furnace, and these are fed by a single current. This is rendered possible by connecting the middle pole of such a system (which is carefully insulated against earth connections) with one of the two terminal poles. For this union a conductor of very high resistance is employed.

This device allows of the following sequence of changes in the alternation of the current employed. At a given instant the entire voltage is brought to bear at the interval between two electrodes, where the arc has been interrupted. As soon as the arc is re-established the tension at that point sinks notably. The entire voltage is then directed upon the poles separated by the high resistance. At these, however, are also poles for the companion arc, a tension nearly as high as that available for kindling the first arc is now active in kindling the second arc. In the instant when the latter is formed the circuit is completed through the two electric flames and the voltage is exerted in creating the two sheets of flame.

By an additional device a number of furnaces can be linked in the same circuit. This consists in the use of an ancillary electric current of very high electromotive force but of low power. By an ingenious switching method this secondary current comes into play as high tension is needed for kindling arcs, but is shut off as the main current develops the several sheets of flame. This method overcomes the difficulty arising from the fact that a much higher electromotive force is required for kindling an arc than for its maintenance when once kindled; in consequence, the energy of the current can be devoted almost exclusively to the maintenance of the flame, the central feature of the manufacturing process. The gas stream leaves the furnace at a temperature of about 1000°C . It is cooled, the nitric oxide is transformed into peroxide and the latter changed into nitric acid, much as described previously in connection with methods now used in Norway. The heat of the furnace gases is utilized in heating the air blast forced into the furnaces and in evaporating the solutions of nitric acid, of nitrites, or of nitrates obtained as final products. Thus far nitric acid is almost the sole product, as nearness to extensive markets renders it much more profitable than any form of nitrate at current prices. A system of pipes and towers of earthenware is used for the acid formation and absorption. The strength of the acid issuing from the towers ranges from 35% to 40%, it is concentrated to a 60% acid by the aid of the heat of the furnace gases. The last traces of oxides in the current of gases issuing from the absorption towers are extracted by forcing the

stream through a solution of alkaline hydrates and transforming the oxides into nitrites, as previously described. The industrial operation yields 60 grams of anhydrous nitric acid, HNO_3 , per kilowatt hour.

The Pauling process combines a much greater variety of clever devices to utilize the electric current than do the rival methods and yet from a mechanical standpoint it is necessarily simple in constructive features, capable of easy control, and involves only slight expense for wear and tear. The rapidity of cooling the gases issuing from the zone of maximum temperature is distinctively greater than in the other two processes. It may ultimately prove a formidable rival of the Norwegian systems.

A series of five absorption towers are next traversed by the current. Each tower contains 250 tons of fragments of acid-resisting brick. A current of water is forced to pass successively from the final tower of the series to the first tower. The dilute acid secured from the five towers shows a constantly increasing strength—from 10° Baumé to 15° , to 20° , and finally to 30° . The last-mentioned strength corresponds to 40% of HNO_3 .

A higher concentration is secured by conducting the 40% acid into porcelain vessels, which are placed in a main traversed by a part of the hot gases issuing from the furnaces. This current carries along not only the water which is evaporated but also a small amount of acid. The acid vapors are condensed by directing the current through coils of earthenware pipe. The dilute acid thus formed is added to the stream passing through the absorption towers, while the gas current on leaving the condenser enters the oxidation chambers. By this method a 50% acid is easily obtained. It is possible to secure a 60% acid by forcing the concentration, but as a rule 50% acid is manufactured. The 60% acid is transformed in these works into a 98% nitric acid by adding double its weight of 92% sulfuric acid and distilling. The product thus secured contains only 0.06% of nitrous vapors. A tower filled with fragments of lava and heated externally is used in this operation. The mixture of the two acids is driven into the tower in the form of spray. Nitric acid in the form of vapor escapes from the top of the tower and is condensed. At the base of the tower 80% sulfuric acid flows out. It is concen-

trated by evaporation and used repeatedly.

In these works, and also in the works in Tyrol, H. Pauling's electrolytic method for concentrating nitric acid (D. R. P. 180052) has been employed. This method is an ingenious one and comparatively simple. It may be destined to play a rôle of considerable importance in the production of 98% acid from the dilute nitric acid obtained by the oxidation of atmospheric nitrogen. At present the cost of the electric energy consumed appears to be too high to warrant the use of the process on a commercial scale. The operation is so conducted that the oxides of nitrogen formed on the cathode during the electrolysis of nitric acid are conducted directly into the portion of the acid surrounding the anode. Here they are oxidized to nitric acid by the nascent oxygen liberated on the anode. Eventually the acid at this point attains the maximum concentration.

The gases leaving the final absorption tower at La Roche-de-Rame are conducted through sand filters to insure the condensation of traces of acid. They then pass through a series of towers charged with sodium carbonate solution. A 20% sodium nitrite solution is thus obtained. It is evaporated with the aid of the heat given off by the furnace gases. The crystals thus secured contain 95% nitrite and 3% nitrate.

The process yields 60 grams of HNO_3 per kilowatt hour.

In a more recent process¹ the gases formed in the electric combustion of air are passed, after traversing an absorbing apparatus acting in the well-known way, through sulfuric acid, and employ the nitrous vitriol thus obtained for drying the cooled gases of the reaction in front of the oxidizing space. This acid is then brought again to the concentration required for oxidizing the remaining gases by the heat of the furnace gases. The nitrous gases, remaining after the previous oxidation and intensive absorption, are mixed, according to whether they contain an excess of NO or of NO_2 , with part of the gases leaving the oxidizing space, or else with a corresponding portion of the non-oxidized furnace gases, in such proportions that for each NO there is a

1. D. R. P. 244840, 246712; abst. C. A. 1912, **6**, 2213, 2504; Chem. Zentr. 1912, **83**, I, 1162, 1872; Chem. Ztg. Rep. 1912, **36**, 234, 302; Wag. Jahr. 1912, **56**, I, 419, 420; Zts. ang. Chem. 1912, **25**, 858, 1648; Zts. Schiess. Spreng. 1912, **7**, 226, 248. U. S. P. 1057977, 1061630; abst. C. A. 1913, **7**, 2288.

molecule of NO_2 present, or vice versa. The gaseous mixture is exposed to absorption by alkaline absorbents, sulfuric acid, or similar reagents. The sulfuric acid, after being saturated with NO and NO_2 , or N_2O_3 , is denitrated in special apparatus, then again concentrated and again used for absorption, conducting the nitrous gases coming from the denitrating apparatus into the principal absorbing apparatus.

The nitrous gases produced by the combustion of the air, after oxidation and absorption, are treated with sulfuric acid¹ in a tower for the absorption of the residual gases, the nitrous sulfuric acid thus obtained being used in the tower for drying the gases, it being at the same time denitrated. Complete denitration is effected in the plant, and the acid returned to the concentrating tower from which the concentrated acid is returned to the absorbing tower. The gases pass through a condensing plant through which a part of the water is removed before they pass into the drying tower.

In another modification,² the stream of nitrous gases to be absorbed is met by an opposing stream of lye, which separates some of the resultant nitrite from the lye at a point in the common path of the stream. In some instances,³ in the manufacture of nitric acid from mixtures of nitrogenous gases and water, the process may be advantageously modified by artificially cooling the mixture to a temperature of 0° or lower.⁴ In another deviation of the main process,⁵ the air or air saturated with oxygen, is heated above 1200° , and as soon as the reaction has taken place the temperature of the mixture is rapidly reduced by passing the vapors over refrigerating or cooled surfaces.

Decomposition of nitrogen oxides formed by the combina-

1. E. P. 22320, 1910; abst. C. A. 1911, **5**, 2920; J. S. C. I. 1911, **30**, 84; Chem. Ztg. Rep. 1911, **35**, 66. E. P. 14121, 1911; abst. C. A. 1913, **7**, 221; J. S. C. I. 1911, **30**, 1252. E. P. 14122, 1911; abst. C. A. 1913, **7**, 221; J. S. C. I. 1911, **30**, 1252. D. R. P. 134932, 1911; abst. C. A. 1911, **5**, 3612; Mon. Sci. 1903, **59**, 713; 1904, **61**, 56; Chem. Centr. 1902, **73**, II, 1023; Chem. Ztg. Rep. 1902, **26**, 970; Chem. Zts. 1903, **2**, 283; Jahr. Chem. 1902, **55**, 1901; Wag. Jahr. 1902, **48**, II, 271. Swiss. P. 57531, 1911.

2. U. S. P. 1061630, 1913; abst. C. A. 1913, **7**, 2288. E. P. 9884, 1910; abst. C. A. 1911, **5**, 2313, 2419; J. S. C. I. 1910, **29**, 1157. Can. P. 125224, 1910; abst. C. A. 1910, **4**, 1057.

3. E. P. 7871, 1906; abst. J. S. C. I. 1906, **25**, 758.

4. E. P. 23385, 1908; abst. C. A. 1910, **4**, 2190; J. S. C. I. 1910, **29**, 88.

5. E. P. 365070, 1906; abst. C. A. 1907, **1**, 2327; Mon. Sci. 1907, **67**, 94; 1911, **75**, 571.

tion of nitrogen and oxygen at high temperatures,¹ is prevented by allowing the reaction mixture to expand without fall of temperature. For this purpose the reaction chamber in which the combination is allowed to take place, is connected to a vacuum chamber, and if the heat transmitted from the chamber is not sufficient to maintain the temperature of the expanded gases which are heated by conduits in the wall or by a flame arc.

In the concentration of nitric acid according to H. Pauling,² it is preferable to employ the diluted nitric acid as free as possible from organic substances, nitrogen oxides and nitrosulfuric acid. From a mixture of one part of 48% HNO_3 and two parts of 94% sulfuric acid, it is easy to continuously obtain 96%–98% HNO_3 , without any substantial amount of weaker acid remaining. According to his French patent,³ nitric acid of 30% when gradually passed through a series of evaporators, acid up to 68% is obtained. These vapors are passed through dephlegmators at various heights. Where a portion of the concentrated nitric acid is added to the nitric-sulfuric acid mixture, it is possible to obtain any desired concentration up to 98% HNO_3 .

Other Nitrogen Fixation Processes. In the recently described processes of H. Gould-Adams, J. Partington and E. Rideal,⁴ nitrates are produced by the absorption of nitrogen oxides (such

1. E. P. 22319, 1910; abst. J. S. C. I. 1911, **30**, 685.

2. U. S. P. 993868, 1031864; abst. Mon. Sci. 1912, **77**, 18; Chem. Ztg. Rep. 1911, **35**, 342; C. A. 1912, **6**, 2676. U. S. P. 1031865, 1074287, 1079541; abst. C. A. 1912, **6**, 2676; 1913, **7**, 3821; 1914, **8**, 405; Mon. Sci. 1913, **79**, 3; 1914, **81**, 27. Aust. P. 48815, 48816; abst. Zts. Schiess. Spreng. 1911, **6**, 377. E. P. 450448, 463859; abst. C. A. 1913, **7**, 2999; 1914, **8**, 2927; Chem. Ztg. Rep. 1913, **37**, 281; 1914, **38**, 310. D. R. P. 257809; abst. C. A. 1913, **7**, 2458; Chem. Zentr. 1913, **84**, I, 1245; Chem. Ztg. Rep. 1913, **37**, 166; Wag. Jahr. 1913, **59**, I, 434; Zts. ang. Chem. 1913, **26**, 235; Zts. Schiess. Spreng. 1913, **8**, 178. D. R. P. 274165; abst. C. A. 1914, **8**, 2930; Chem. Zentr. 1914, **85**, I, 1981; Chem. Ztg. Rep. 1914, **38**, 323; Wag. Jahr. 1914, **60**, I, 355; Zts. ang. Chem. 1914, **27**, 397.

3. See also: Norsk. Hydro-Elektrisk Kvaestofaktieselskab, U. S. P. 1200334, 1916; abst. J. S. C. I. 1916, **35**, 1156. E. P. 451812, 1913; 477726, 1915; abst. J. S. C. I. 1916, **35**, 601; C. A. 1916, **10**, 1582; Mon. Sci. 1914, **81**, 7. D. R. P. 206949, 1907; abst. C. A. 1909, **3**, 1919; Mon. Sci. 1912, **77**, 90; Chem. Zentr. 1909, **80**, I, 1127; Chem. Ztg. Rep. 1909, **33**, 137; Chem. Zts. 1909, **8**, No. 1184; Wag. Jahr. 1909, **55**, I, 417; Jahr. Chem. 1909, **62**, 581; Zts. ang. Chem. 1909, **22**, 551; Zts. Schiess. Spreng. 1909, **4**, 95. Nor. P. 20607, 1910; abst. C. A. 1912, **6**, 1971; Chem. Ztg. Rep. 1911, **35**, 129; Mon. Sci. 1914, **81**, 83. Nor. P. 27550, 1917; abst. C. A. 1917, **11**, 1731. Jap. P. 30228, 1916; abst. C. A. 1917, **11**, 1731.

4. E. P. 126715, 126716, 126717, 129699, 1919; abst. J. S. C. I. 1919, **38**, 499, 681-A; C. A. 1919, **13**, 2980.

as the products of the electric arc, oxidation of N or of the oxidation of ammonia) in solutions or suspensions of alkali, alkaline earth, or the copper or zinc compounds, wherein a series of absorption towers or chambers are employed, the gas being passed through until the solution contains only nitrate. The unabsorbed oxides are oxidized to NO_2 , and led into another absorption chamber.¹

B. Halvorsen² obtains nitrous gases in concentrated form from dilute gaseous mixtures by absorption in a dry mixture composed of NaOH and an oxide as ferric, zinc or aluminium, and then heating the products with steam. This produces nitric acid and concentrated nitrous gases, and prepares the residue for further treatment use as an absorbent.

K. Quinan³ manufactures nitric acid by the oxidation of nitrogen or ammonia, the nitrogen oxides being absorbed by water which is distributed over permeable diaphragms, through which the gases pass without appreciable percolation of the liquid. The gaseous reactions take place in chambers of such a volume as to give sufficient time for the reaction. Improved control of temperatures and lower cost of plant as compared with towers is claimed.

In the G. Toniolo process,⁴ of nitric acid manufacture, by absorbing nitrogen oxides in water in a series of towers in counter-current, strong cooling of the acid passing from tower to tower being effected by artificial refrigeration so that the acid entering each tower may be in the neighborhood of its freezing point; the acid entering the last tower may be $4^\circ\text{--}5^\circ$, the earlier towers carrying 65% acid being around 25° .⁵ The devices perfected by A. Lindblad⁶ are so arranged that the material to be combined with N is charged, together with a gas containing N, into an electric furnace open at the top in conical form and provided near

1. S. Eyde, E. P. 28614, 1904; abst. J. S. C. I. 1905, **24**, 619. Saltpetresäure Ind. Ges. E. P. 9884, 1910; abst. J. S. C. I. 1910, **29**, 1157.

2. U. S. P. 1316950, 1919; abst. C. A. 1919, **13**, 2978.

3. E. P. 131029, 1918; abst. J. S. C. I. 1919, **38**, 718-A; C. A. 1920, **14**, 97.

4. E. P. 121635, 1917; abst. J. S. C. I. 1919, **38**, 104-A; C. A. 1919, **13**, 892.

5. See Norsk. Hydro-Elektrisk Kvaestofaktieselskab, U. S. P. 1273991, 1918; abst. J. S. C. I. 1918, **37**, 622-A. E. P. 116495, 1918; abst. J. S. C. I. 1919, **38**, 622-A.

6. Swiss P. 78794, 1918; abst. C. A. 1919, **13**, 1285.

the narrowed portion with an electrode, so that the material serves to conduct the current to the walls of the furnace as a resistant charge.

In the absorption of nitrogen oxides in an upward spray of water and air in an empty tower in which the spray is produced by a jet of compressed air opening below the surface of water in the bottom of the tower,¹ the jet is surrounded by an inverted funnel having holes, the upper part of the funnel being above the level of the water. This arrangement is designed to prevent irregularities in the working of the jet owing to variations in the level of water.

Oxidation of Ammonia to Nitric Acid.² In 1839 F. Kuhlmann³ observed that when a mixture of ammonia and air is led over platinum sponge in a glass tube heated to about 300°, the platinum continues to glow, and a mixture of nitrous and nitric acids result with an excess of ammonia. When the mixture was passed through a heated porcelain tube, the reaction—although apparent—was slow. It was found that platinum black was less efficient than the sponge, and elemental copper, nickel, iron and copper hydroxide still less energetic. W. Moldenhauer and O. Wehrheim⁴ observed that cyanogen and hydrocyanic acid are more readily oxidized than ammonia.

K. Kraut⁵ and others⁶ have recorded that red fumes result

1. B. Dawson, E. P. 120869, 1918; abst. C. A. 1919, **13**, 640. In this connection see also The Air Reduction Co., Can. P. 188363, 1920. E. Ashcroft, Can. P. 196490, 1920; abst. C. A. 1920, **14**, 603. Bueb, J. Gasbel, 1919, **62**, 2; abst. C. A. 1920, **14**, 598. A. Crowell, Jr., U. S. P. 1321892; abst. C. A. 1920, **14**, 324. C. Gray and E. Hagenlocher, Elec. World, 1919, **74**, 1052; abst. C. A. 1920, **14**, 496. A. Lipinski, Can. P. 197405, 1920. E. Lof, Elec. World, 1920, **75**, 148; abst. C. A. 1920, **14**, 496. L. Mage, E. P. 134229, 1919; abst. C. A. 1920, **14**, 803. E. Maxted, Chem. Age, 1920, **2**, 6; abst. C. A. 1920, **14**, 598. Nitrogen Co., D. R. P. 258295; abst. Chem. Ztg. 1913, **37**, 336. J. Saetersmoen and C. Rabot, Techn. Ukeblad, 1919, **75**, 223; abst. C. A. 1920, **14**, 496. J. usšnes gaz. 1919, **43**, 266, 273, 295; abst. C. A. 1920, **14**, 313.

2. Considerable of the data embodied in this topic has been abstracted from "Memorandum on the Oxidation of Ammonia to Nitric Acid," N. P. C. Doc. No. 62, by J. Partington, January 15, 1917.

3. Ann. 1839, **29**, 281; Mem. Soc. Sci. Lille, 1838, 88; abst. Berz. Jahr. 1840, **19**, 178.

4. Zts. ang. Chem. 1914, **27**, 334; abst. C. A. 1915, **9**, 417; J. S. C. I. 1914, **33**, 748.

5. Ann. 1865, **136**, 69; abst. Zts. Chem. 1865, **8**, 637; Ann. Chim. Phys. 1866, (4), **6**, 479; Bull. Soc. Chim. 1866, **5**, 206; Phil. Mag. 1865, (4), **30**, 448; Chem. News, 1865, **12**, 231; Jahr. Chem. 1865, **18**, 156.

6. A. Hofmann, Ann. 1860, **115**, 285. W. Heintz, Ann. 1864, **130**, 102. S. Lupton. Chem. News, 1878, **38**, 227. W. Hodgkinson and F.

with intermittent explosions when a hot platinum spiral is hung inside a flask containing ammonia, and through which oxygen is passed. E. Aubertin¹ proposed as catalysts, chromium oxides and chromates; T. du Motay advocated² manganates, permanganates, bichromates and alkali plumbites; Siemens & Halske³ used an ozonizer, while H. Schwarz⁴ employed sodium manganate, and R. Marston⁵ obtained best results by passing air and ammonia over hot copper.

D. Menighini,⁶ and V. Reinders and A. Catz⁷ employed various oxides, but without concordant results. W. Ostwald in 1902 published the results of his researches on the catalytic oxidation of ammonia by platinum, for which patent protection was granted.⁸ Ostwald was unsuccessful in obtaining a German patent, on account of the priority work of F. Kuhlmann.⁹

K. Schick⁹ employed platinized, glazed porcelain tile, which was claimed to have a longer life than platinum sponge. A factory at Gerthe, Westphalia¹⁰ was erected, the Nitrate Products Co., absorbing the Ostwald patents for England.¹¹ K. Kaiser¹² patented a method of pre-heating the air before mixing with

Lowndes, Chem. News, 1888, **58**, 27. D. Hammick, Chem. News, 1916, **114**, 285; abst. C. A. 1917, **11**, 420.

1. E. P. 1181, 1871.

2. Deut. Ind. Ztg. 1871, 388; abst. Chem. Tech. Rep. 1871, **10**, 11, 127; Wag. Jahr. 1871, **17**, 260. E. P. 491, 2231, 1871.

3. D. R. P. 85103; abst. Ber. 1896, **29**, 245; Mon. Sci. 1896, **48**, 72; Chem. Tech. Rep. 1896, **35**, 195; Wag. Jahr. 1896, **42**, 410; Chem. Ztg. 1896, **20**, 204; Chem. Centr. 1896, **67**, 1, 1216; Zts. ang. Chem. 1896, **9**, 75; Jahr. Chem. 1896, **49**, 414.

4. Dingl. Poly. 1875, **218**, 219.

5. E. P. 19074, 1900; abst. Chem. Ztg. 1902, **26**, 206; J. S. C. I. 1901, **20**, 1200; Mon. Sci. 1902, **58**, 154.

6. Gazz. chim. ital. 1912, **42**, 1, 126; 1913, **43**, 1, 81; abst. J. S. C. I. 1912, **31**, 383; 1913, **32**, 230; Chem. Ztg. Rep. 1913, **37**, 378.

7. Chem. Weekblad, 1912, **9**, 47; abst. Chem. Zentr. 1912, **83**, 1, 708; J. S. C. I. 1912, **31**, 280.

8. E. P. 698, 8300, 1902; abst. Chem. Ztg. 1903, **27**, 457; J. S. C. I. 1902, **21**, 548. F. P. 317544. Swiss P. 25881. U. S. P. 858904, 1907.

9. Chemische Fabrik Griesheim Elektron, E. P. 13954, 16885, 1907; abst. J. S. C. I. 1908, **27**, 447. F. P. 380884, 1907; abst. J. S. C. I. 1908, **27**, 22. U. S. P. 971149, 1910. E. P. 14448, 1911.

10. Elec. Rev. 1911, 69, 531; Chem. Trade J. and Chem. Engineer, 1915, **56**, 553.

11. Chem. Trade J. 1915, **56**, 45, 533; **57**, 26; Sci. Amer. Suppl. Sept. 25, 1915.

12. E. P. 20325, 1910; abst. J. S. C. I. 1910, **29**, 1377; C. A. 1911, **5**, 2707; Chem. Ztg. Rep. 1911, **35**, 3. F. P. 435397, 1912; abst. Mon. Sci. 1913, **79**, 132. See W. Hochmann, Pharm. Inst. 1911, **8**, 81; abst. Chem. Zentr. 1912, **83**, 1, 689.

ammonia, and passing over a platinum catalyst, iridium gauze,¹ being used in a subsequent process.

F. Bayer & Co.² pass the ammonia over the catalyst at 600° 750° at high velocity.³ The Badische Co. proposed the use of oxides of the iron group, the catalyst being in the form of lumps⁴, bismuth oxide,⁵ tellurium⁶ or platinum and lead.⁷ A. Frank and N. Caro⁸ advise the use of ceria and thoria; L. Jones, D. Morton

1. E. P. 21035, 1911; abst. C. A. 1913, **7**, 1405; J. S. C. I. 1912, **31**, 775.
2. D. R. P. 168272, 1902; abst. Wag. Jahr. 1906, **52**, I, 419; Chem. Centr. 1906, **77**, I, 1198; Chem. Ztg. 1906, **30**, 125; Zts. ang. Chem. 1906, **19**, 1941; Jahr. Chem. 1905-1908, I, 1777; Chem. Zts. 1906, **5**, 344; Zts. Schiess. Spreng. 1906, **1**, 103. E. P. 18594, 1903; abst. J. S. C. I. 1904, **23**, 787. E. P. 460859; abst. C. A. 1914, **8**, 2464; Mon. Sci. 1914, **81**, 75; Chem. Ztg. Rep. 1914, **38**, 237. It. P. 124405; abst. Chem. Ztg. 1913, **37**, 228.
3. H. Maxted, J. S. C. I. 1917, **36**, 777; Engineering 1917, **104**, 133; Chem. Trade J. 1917, **61**, 72; C. A. 1917, **11**, 2718.
4. U. S. P. 1094182, 1914. E. P. 2414, 1908; 9263, 1913; 13687, 13848, 1914; 7651, 13297, 13298, 1915. E. P. 398738, 1909. E. P. 411446, 416877, 417940, 418059, 418287, 418434, 425009, Add. 15984, 16622, 1912; 431298, Add. 16353, 1912; 458950, 464237, 466303; abst. Mon. Sci. 1913, **79**, 74, 83, 85, 86; 1914, **81**, 72; 1916, **83**, 14; Chem. Ztg. 1911, **35**, 342. D. R. P. Ann. B-16319. D. R. P. 233729, 1910; 283824, 1915. Swiss P. 69951, 72690. G. Taylor, J. Ind. Eng. Chem. 1919, **11**, 1121; abst. J. S. C. I. 1920, **39**, 61-A. G. Taylor and I. Knapp, E. P. 134237, 1918; abst. C. A. 1920, **14**, 803. P. Rowlands, E. P. 7740, 1912; abst. Chem. Ztg. 1913, **37**, 336. F. Müller, D. R. P. Ann. M. 45598; abst. Chem. Ztg. 1913, **37**, 302. Q. Moore, J. Cunningham and J. Stokes, Belg. P. 251147; abst. Chem. Ztg. 1913, **37**, 228. C. Montgomery and E. Royston, E. P. 131609, 1916; abst. C. A. 1920, **14**, 318. E. Maurer, Zts. anorg. Chem. 1919, **108**, 273; abst. J. S. C. I. 1920, **19**, 61-A. A. Matignon, Swiss P. 57539; abst. Chem. Ztg. 1913, **37**, 44. A. Lowenstein, U. S. P. 1322251, 1919; abst. C. A. 1920, **14**, 317; J. S. C. I. 1920, **14**, 21-A. E. Haslup, E. P. 135889, 1918; abst. J. S. C. I. 1920, **39**, 110-A. See U. S. P. 1310478, 1310479, 1919; abst. J. S. C. I. 1919, **38**, 629-A. B. Halvorsen, U. S. P. 1316950; abst. J. S. C. I. 1919, **38**, 817-A. H. Goold-Adams, J. Partington and E. Rideal, E. P. 135224, 1917; abst. J. S. C. I. 1920, **39**, 62-A. R. Gardiner, U. S. P. 1328082, 1920; abst. C. A. 1920, **14**, 803. R. Dawson, E. P. 123344, 1917; abst. Chim. Ind. 1920, **3**, 213. A. Classen, U. S. P. 1322291, 1919; abst. C. A. 1920, **14**, 317. I. Cederberg, H. Backstrom and C. Kyhlberger, E. P. 127063, 127064; abst. C. A. 1919, **13**, 2422, 2423; Chim. Ind. 1920, **3**, 213. E. Briner, Helv. Chim. Acta, 1919, **2**, 162; abst. Chim. Ind. 1920, **3**, 211. C. Bosch, Zts. Elektrochem. 1918, **24**, 361; abst. C. A. 1920, **14**, 792. J. Baumann, Chem. Ztg. 1919, **43**, 466; abst. C. A. 1920, **14**, 800. P. Starke, Can. P. 190746, 190747, 190748, 1920. W. Bousfield and Nobel's Explosives Co., E. P. 131642, 1918; abst. C. A. 1920, **14**, 316.
5. E. P. 13848, 1914; 7651, 1915; abst. J. S. C. I. 1915, **34**, 799; 1916, **35**, 1015; Chem. Ind. 1916, **22**, 117; Mon. Sci. 1917, **83**, 76.
6. E. P. 13297, 1915; abst. J. S. C. I. 1916, **35**, 1108; Mon. Sci. 1917, **84**, 186; Chem. Ind. Ann. Rep. 1917, **1**, 186.
7. E. P. 13298, 1915; abst. Mon. Sci. 1917, **84**, 186; J. S. C. I. 1916, **35**, 1015; C. A. 1917, **12**, 528.
8. D. R. P. 224329; abst. Wag. Jahr. 1910, **56**, I, 485; Chem. Zentr. 1910, **81**, II, 511.

and G. Terziev propose to use magnesium, aluminium, zinc or cadmium plumbites;¹ and Wendriner prefers uranium as the catalyst.²

The actual mechanism of the reaction in the oxidation is rather obscure, and has been variously represented as NO , N_2O_3 , NO_2 and HNO_3 . It would appear, however, from the high temperature employed that the initial product is NO .³ W. Ostwald states only sufficient air should be employed to form NO_2 ,⁴ while M. Rohmer maintains⁵ that only sufficient air to remove the H from the NH_3 should be admitted. After removal of the oxides, pure nitrogen for ammonia synthesis remains.⁶ The use of increased pressure after oxidation had been considered preferable.⁶ The yield appears to be increased⁷ if the hot gases from the contact mass are rapidly cooled. Although iron is resistant to nitric vapors, parts of the apparatus exposed to them are preferably made of aluminium, stoneware or nickel steel,⁸ or ferrochromium containing more than 25% Cr.⁹ Those parts exposed to the liquid nitric acid are best made of silica.¹⁰ Estimates of the cost of production vary greatly.¹¹

The above skeleton outline has been greatly extended by the researches of E. Briner and A. Baerfuss,¹² Verein Chemischer Fabriken in Mannheim,¹³ W. Adam,¹⁴ J. Baumann,¹⁵ A. Besson,¹⁶

1. U. S. P. 1037261, 1912; abst. C. A. 1912, **6**, 3498; Mon. Sci. 1913, **79**, 5.
2. Chem. Ind. 1911, **34**, 456; 1914, **37**, 205.
3. C. Matignon, Chem. Trade J. and Chem. Eng. 1914, **54**, 179; Chem. Ztg. 1914, **38**, 894, 909. Technique Moderne, 1913, 297. A. Richardson, J. C. S. 1887, **51**, 397.
4. U. S. P. 858904. E. P. 698, 8300, 1902; 7909, 1908. D. R. P. 207154, 1907; abst. J. S. C. I. 1909, **28**, 365. W. Ostwald and E. Brauer, F. P. 317544. Swiss P. 25881; Chem. Ztg. 1903, **27**, 457.
5. U. S. P. 1006392, 1006393, 1914; abst. C. A. 1914, **8**, 2228.
6. F. P. 453845; abst. Chem. Ztg. Rep. 1913, **37**, 474.
7. The Societe General des Nitrures, F. P. 473618; abst. Mon. Sci. 1916, **83**, 81; Chem. Ztg. Rep. 1916, **40**, 146.
8. W. Ostwald, D. R. P. 207154, 1906; abst. J. S. C. I. 1909, **28**, 365.
9. Chemische Fabrik Griesheim-Elektron, F. P. 14448, 1914.
10. R. Seligmann and P. Williams, J. S. C. I. 1916, **35**, 665.
11. Iron and Coal Trades Review, May 22, 1913; Chem. Ind. 1914, **37**, 265; Chem. Trade J. 1914, 283. Met. Chem. Eng. 1916, **14**, 418.
12. Helvetica Chim. Acta, 1919, **2**, 95; abst. J. S. C. I. 1919, **38**, 219-A; G. A. 1919, **13**, 1282. J. Chim. Phys. 1919, **17**, 71; abst. J. S. C. I. 1919, **38**, 572-A. E. Briner, Hel. Chim. Acta, 1919, **2**, 162; J. S. C. I. 1919, **38**, 284. E. Briner and E. Mettler, J. Chim. Phys. 1908, **6**, 137; abst. J. S. C. I. 1908, **27**, 575.
13. D. R. P. 311234, 1914; abst. J. S. C. I. 1919, **38**, 462-A. E. P. 12600, 1914.
14. Chem. Trade J. 1918, **62**, 181; abst. J. S. C. I. 1918, **37**, 179-A.
15. Chem. Ztg. 1919, **43**, 466; abst. J. S. C. I. 1919, **38**, 716-A.
16. Compt. rend. 1911, **152**, 1850; abst. J. S. C. I. 1911, **30**, 892.

J. Billiter,¹ C. Bromley,² I. Uederberg, H. Backstrom and G. Kyhlberger,³ H. Le Chatelier,⁴ A. Classen,⁵ G. Claude,⁶ H. Creighton,⁷ A. Crossley,⁸ B. Crowell,⁹ R. Davis,¹⁰ O. Dieffenbach,¹¹ W. Easton,¹² J. Fischler,¹³ P. Fox,¹⁴ D. Gaillard,¹⁵ General Chemical Co.,¹⁶ R. Glaser,¹⁷ Goold (Balfour-Guthrie Investment Co.),¹⁸ H. Greenwood,¹⁹ Gros and Bouchardy,²⁰ L. Hamburger,²¹ H. Hampel and R. Steinau,²² Hanna and Major,²³ A. Henwood,²⁴ H. Hoyer-

1. *Nernst-Festschrift*, 86; abst. *Chem. Zentr.* 1912, **83**, II, 803; *J. S. C. I.* 1912, **31**, 919.
2. *Power*, 1919, **49**, 424, 482, 558; abst. *C. A.* 1919, **13**, 2738.
3. *E. P.* 127063, 127064, 1918; abst. *C. A.* 1919, **13**, 2423; *J. S. C. I.* 1919, **38**, 446, 535-A. *F. P.* 488821, 488822. In this connection see *E. P.* 12604, 1893; 2461, 1902; 5835, 17411, 28167, 1911; 16903, 1913; abst. *C. A.* 1912, **6**, 2500; 1913, **7**, 403, 1958; 1915, **9**, 358.
4. *Compt. rend.* 1917, **164**, 588; abst. *J. S. C. I.* 1917, **36**, 545. *F. P.* 313950; abst. *Mon. Sci.* 1903, **59**, 14.
5. *U. S. P.* 1256875, 1918. *E. P.* 7866, 1914. *D. R. P.* 288159.
6. *Compt. rend.* 1919, **168**, 1001; abst. *C. A.* 1919, **13**, 1902.
7. *J. Frank. Inst.* 1919, **187**, 705; abst. *C. A.* 1919, **13**, 1622. *Cf. C. A.* 1919, **13**, 1130, 1372.
8. *Engineering*, 1912, 599. *A. Morvillez, Ind. chim. rev. Prod. Chim.* 1918, **5**, 101; abst. *C. A.* 1918, **12**, 1682.
9. *Elec. World*, 1919, **73**, 281; abst. *C. A.* 1919, **13**, 537. *J. Ellbert, U. S. P.* 1313886; abst. *C. A.* 1919, **13**, 2744.
10. *Science*, 1919, **40**, 620; abst. *C. A.* 1919, **13**, 3012. *R. Davis and L. Olmstead, Science*, 1919, **49**, 620; abst. *C. A.* 1919, **13**, 3012.
11. *Chem. Ind.* 1914, **37**, 265; abst. *J. S. C. I.* 1914, **33**, 590. *E. Donath, Chem. Ind.* 1914, **37**, 513. *C. Dafert, Oest. Chem. Ztg.* 1912, 56.
12. *J. A. C. S.* 1903, **25**, 1042; abst. *J. S. C. I.* 1903, **22**, 1258. *A. Chappero, Ind. Chim. min. met.* 1919, **6**, 41; abst. *C. A.* 1919, **13**, 1244.
13. *Chem. Ztg.* 1919, **43**, 11; abst. *C. A.* 1919, **13**, 1518. See also *C. A.* 1919, **13**, 1128.
14. *J. Ind. Eng. Chem.* 1917, **9**, 737; abst. *J. S. C. I.* 1917, **36**, 1005. *C. Thorsell and H. Lunden, U. S. P.* 1288755, 1288756; abst. *C. A.* 1919, **13**, 641. *E. P.* 132625, 132626, 132882, 132883, 136772; abst. *C. A.* 1920, **14**, 319, 320. *J. S. C. I.* 1920, **39**, 89-A. *Can. P.* 189600 to 189604.
15. *J. Ind. Eng. Chem.* 1919, **11**, 745; abst. *J. S. C. I.* 1919, **38**, 860-A; *C. A.* 1919, **13**, 1989. *H. Fischer, Ber. Deut. Bot. Ges.* 1917, **35**, 423; *Abstracts of Bacteriology*, **2**, 269; abst. *C. A.* 1919, **13**, 1083. See also *C. A.* 1917, **11**, 2251.
16. *E. P.* 120546, 124759, 124762, 1918; abst. *C. A.* 1919, **13**, 643, 1747, 1748. *H. Niggemann, "Ges. Abhandl. zur Kenntnis der Kohle,"* 1917, I, 289; *Chem. Zentr.* 1919, **90**, II, 615; *J. S. C. I.* 1919, **38**, 532-A.
17. *Feuerungstechnik*, 1917, **6**, 3; abst. *Zts. ang. Chem.* 1918, **31**, II, 248; *C. A.* 1919, **13**, 995; *J. S. C. I.* 1918, **37**, 621-A.
18. *E. P.* Appl. 7403, 1919; abst. *J. S. C. I.* 1919, **38**, 238-A. *A. Cocking and Kynoch, Ltd., E. P.* 125444, 1916; abst. *C. A.* 1919, **13**, 2258.
19. *U. S. P.* 1312534, 1919; abst. *C. A.* 1919, **13**, 2429. *Greenwood and Tate, E. P.* 7323, 1919; abst. *J. S. C. I.* 1919, **38**, 238-A.
20. *E. P.* Appl. 4490, 4600, 1919; abst. *J. S. C. I.* 1919, **38**, 161, 205-A.
21. *Chem. Weekblad*, 1918, **15**, 931; abst. *C. A.* 1918, **12**, 2283.
22. *Chem. Ztg.* 1918, **42**, 489; abst. *J. Ind. Eng. Chem.* 1919, **11**, 368; abst. *C. A.* 1919, **13**, 1128. *Chem. Ztg. Rep.* 1918, **42**, 594; abst. *J. C. S.* 1919, **115**, 62.
23. *E. P.* Appl. 20974, 1919; abst. *J. S. C. I.* 1919, **38**, 700-A.
24. *U. S. P.* 1309622, 1919; abst. *C. A.* 1919, **13**, 2422.

mann,¹ K. Jellinek,² L. Jones and C. Parsons,³ W. Landis,⁴ F. Liljoroth,⁵ E. Maxted,⁶ F. Metzger,⁷ The Nitrogen Corporation,⁸ Norsk. Hydro-Elektrisk Kvaestofaktieselskab,⁹ E. Orlow,¹⁰ C. Parsons,¹¹ R. Parsons, H. Jenkins and C. I. (1914) Syndicate,¹² J. Partington,¹³ P. Pascal and E. Decarriere,¹⁴ E. Pease,¹⁵ E. Periman,¹⁶ L. Rabinovitz,¹⁷ G. Scagliarini,¹⁸ F. Schreiber,¹⁹ F. Slocum,²⁰ L'Air Liquide, Soc. Anon. pour l'Étude et l'Exploit. des Proc. G.

1. Chem. Ztg. 1902, **26**, 70; abst. J. S. C. I. 1902, **21**, 166.
2. Zts. anorg. Chem. 1911, **71**, 121; abst. J. S. C. I. 1911, **30**, 892.
3. E. P. 132551, 1918; abst. J. S. C. I. 1919, **38**, 817-A. L. Jones, U. S. P. 1307739, 1919; abst. J. S. C. I. 1919, **38**, 575-A; C. A. 1919, **13**, 2259.
4. U. S. P. 1296820, 1919; abst. J. S. C. I. 1919, **38**, 362-A. U. S. P. 1292814; abst. C. A. 1919, **13**, 999. Chem. Met. Eng. 1919, **20**, 470; abst. J. S. C. I. 1919, **38**, 410-A. Met. Eng. 1916, 87; abst. Chem. Ind. 1916, **39**, 156.
5. Chem. Met. Eng. 1918, **19**, 287; abst. J. S. C. I. 1918, **37**, 730-A; C. A. 1918, **12**, 2413.
6. U. S. P. 1296992, 1919; abst. C. A. 1919, **13**, 1625. E. P. 127343, 130023, 130063, 131049; abst. J. S. C. I. 1919, **38**, 499, 680, 718-A; C. A. 1919, **13**, 2422. J. C. S. 1918, **113**, 168, 386; 1919, **115**, 113; abst. J. S. C. I. 1918, **37**, 368-A; 1919, **38**, 219-A; C. A. 1918, **12**, 1443, 2235; 1919, **13**, 1057. J. S. C. I. 1918, **37**, 232-T; abst. C. A. 1918, **12**, 2235. Metall. Eng. 1917, 345. E. Maxted and G. Ridsdale, E. P. 124824, 126083, 1916; abst. J. S. C. I. 1919, **38**, 323, 413-A; C. A. 1919, **13**, 1748, 2259. E. Maxted and T. Smith, E. P. 127845, 1917; 128623, 132571, 1918; abst. J. S. C. I. 1919, **38**, 484, 518, 575, 817-A.
7. U. S. P. 1213314, 1213315, 1213316, 1919; abst. C. A. 1919, **13**, 2742, 2743.
8. N. Zeal. P. 42164, 1919. E. P. 128939, 1919; abst. C. A. 1919, **13**, 2978.
9. E. P. Appl. 21447, 1919; abst. J. S. C. I. 1919, **38**, 700-A. Nor. P. Sept. 13, 1918. D. R. P. 206949, 1907. 289745.
10. J. Russ. Phys. Chem. Soc. 1903, **40**, 659; abst. Chem. Zentr. 1903, **79**, 11, 1499; J. S. C. I. 1908, **27**, 1150.
11. J. Ind. Eng. Chem. 1919, **38**, 497-A.
12. E. P. 130069, 1918; abst. J. S. C. I. 1919, **38**, 608, 680-A.
13. J. S. C. I. 1918, **37**, 337-R; abst. C. A. 1918, **12**, 2665. J. Partington and E. Rideal, E. P. 131942, 1918; abst. J. S. C. I. 1919, **38**, 763-A.
14. Bull. Soc. Chim. 1919, **25**, 489; abst. J. S. C. I. 1919, **38**, 860-A.
15. E. P. 121754, 1917; abst. J. S. C. I. 1919, **38**, 104-A; C. A. 1919, **13**, 904.
16. Proc. Chem. Soc. 1903, **19**, 204; abst. J. S. C. I. 1903, **22**, 1242. See J. S. C. I. 1902, **21**, 116. Proc. Roy Soc. 1905, **76-A**, 167; abst. J. S. C. I. 1905, **24**, 672.
17. U. S. P. 1304707, 1919; abst. C. A. 1919, **13**, 2112; J. S. C. I. 1919, **38**, 575-A.
18. Gazz. chim. ital. 1914, **44**, 543; abst. J. S. C. I. 1914, **33**, 690. See J. S. C. I. 1913, **32**, 138. E. Müller and F. Spitzer, Ber. 1905, **38**, 778, 1188; abst. J. S. C. I. 1905, **24**, 279, 550.
19. Chem. Ztg. 1911, **35**, 943; abst. J. S. C. I. 1911, **30**, 1113.
20. U. S. P. 1315532; abst. J. S. C. I. 1919, **38**, 818-A; C. A. 1919, **13**, 2978.

Claude,¹ P. Starke,² G. Taylor and J. Kapps,³ C. Thorsell and H. Lundén,⁴ A. Wells,⁵ F. Wielgolaski,⁶ C. Zenghelis⁷ and others.⁸

Haber Method for the Synthetic Production of Ammonia.

F. Haber, collaborating with G. van Oordt, published in 1905

1. E. P. 130086, 130087, 130365, 1918; abst. J. S. C. I. 1919, **38**, 690, 718-A.
2. U. S. P. 1256273, 1918; 1306862, 1919. Can. P. 190748, 1919; abst. C. A. 1919, **13**, 2259.
3. U. S. P. 1315534, 1919; abst. C. A. 1919, **13**, 2978; J. S. C. I. 1919, **38**, 818-A. G. Taylor and J. Kapps, J. Ind. Eng. Chem. 1919, **11**, 27; abst. J. S. C. I. 1919, **38**, 132-A. J. Taylor and J. Davis, J. Ind. Eng. Chem. 1917, **9**, 1106; abst. J. S. C. I. 1918, **37**, 54-A. P. Fox, J. S. C. I. 1917, **36**, 1005.
4. U. S. P. 1286838, 1286839, 1288754, 1288756, 1918; abst. C. A. 1919, **13**, 641; J. S. C. I. 1919, **38**, 134, 862-A. Can. P. 189604, 1919; abst. C. A. 1919, **13**, 1520.
5. U. S. P. 1252976, 1918.
6. U. S. P. 1287807, 1287808, 1918; abst. J. S. C. I. 1919, **38**, 150-A.
7. Compt. rend. 1916, **162**, 914; abst. J. S. C. I. 1916, **35**, 835.
8. American Cyanamide Co., U. S. P. 1193796, 1193797, 1193798, 1193799, 1193800, 1916; 1206062, 1206063, 1217247, 1917. Can. P. 161112, 161113, 161391, 161566, 164154, 164820, 165745, 1915; 167104, 172242, 1916; 186910, 186911, 1918; 182260, 1920. T. Aucher, F. P. 485455. S. Bailey, E. P. 19189, 1905. "Bamag," D. R. P. Ann. B. 78607. A. Bambach, F. P. 469331, Chem. Ind. Ann. Rep. 1916, **1**, 118. H. Bernthsen, Mon. Sci. 1914, **81**, 150; J. Ind. Eng. Chem. 1912, 160. Berthelot, Rev. de Metall. 1913, 1010. Buskvold, Span. P. 61367, 1915. H. Cathala, Techn. mol. 1914, 165. G. Coutagne, F. P. 177746; Mon. Sci. 1916, **83**, 87. O. Engles and F. Dürre, D. R. P. 229096, 1908; abst. Chem. Zentr. 1911, **82**, I, 177. F. Foerster and M. Koch, Zts. ang. Chem. 1908, **21**, 2209; 1910, **23**, 2018. P. Guye, F. P. 385569, 385605. D. Helbig, Zts. Elektrochem. 1906, **12**, 550. E. Hene, Chem. Ztg. Rep. 1911, **38**, 317, 342. W. Holwech, Zts. ang. Chem. 1908, **21**, 2131. K. Kaiser, E. P. 20325, 1910; 21035, 1911; abst. Chem. Ztg. Rep. 1911, **35**, 3. F. P. 419782, 1910; 435397, 1912; abst. Mon. Sci. 1913, **79**, 132. J. Kowalski and I. Moscicki, U. S. P. 754147, 1904. M. Leblanc, Zts. Elektrochem. 1906, **12**, 541. H. Lelarge, E. P. 18579, 1913; abst. J. S. C. I. 1914, **33**, 906. G. Lewis and A. Edgar, J. A. C. S. 1911, **33**, 292. G. Lunge and E. Berl, Zts. ang. Chem. 1906, **19**, 807; 1907, **20**, 1713. S. Lupton, Chem. News, 1878, **37**, 227. R. Marston, E. P. 4080, 1899; 19074, 1900; abst. J. S. C. I. 1901, **20**, 1209; Chem. Ztg. 1902, **26**, 206. Meister, Lucius & Brining, E. P. 19032, 1911; 3662, 1913; 28737, 1913. U. S. P. 1145162, 1915. R. Nithack, D. R. P. 95532; abst. Chem. Zentr. 1898, **69**, I, 647; Chem. Ztg. 1898, **22**, 140. Nordyke & Marmon Co., E. P. 1204, 1906; abst. J. S. C. I. 1906, **25**, 536. Oester. Ver. Chem. u. Metall. Prod., D. R. P. 276720. F. Raschig, Zts. ang. Chem. 1904, **17**, 1777; D. R. P. 286122. A. Richardson, J. C. S. 1887, **51**, 397. Scherfenberg & Prager, D. R. P. 202560, 1907. S. Centralstelle f. Wissenschaftlich-Technische Untersuchungen, F. P. 450465; abst. Mon. Sci. 1914, **81**, 6. O. Serpek, D. R. P. 221628, 1907; Zts. ang. Chem. 1913, **26**, 606; Mon. Sci. 1914, **81**, 542; 1915, **82**, 20. Can. P. 145508, 1913; 153563, 154574, 155784, 156533 4-5, 1914; 160853, 166161, 1915; 194795 6-7, 1919; abst. C. A. 1929, **14**, 603. E. P. 10036, 1912; abst. Chem. Ztg. 1913, **37**, 228. Soc. Generale des Nitrures, F. P. 454430, 473618; abst. Chem. Ztg. Rep. 1913, **37**, 590; Mon. Sci. 1914, **81**, 10. Can. P. 156533-4 5, 1914; 164839, 1915; 173693, 1916; 174685, 1917. E. P. 16106, 1912. F. P. 448924, 450140, 450178. It. P. 120985, 124987. Aust. P. 58173, 58193. T. Takeuchi, Chem. Ztg. Rep. 1911, **35**, 408; 1914, **38**, 1015. Waser, Chem. Ztg. 1915, **39**, 460, 761, 782, 848; 1916, Jan. & Feb. See also

and 1906 a series of papers¹ in which the theoretical conditions for the successful solution of this problem were stated. The necessity for relatively low temperature operation was clearly demonstrated. It was established that above a dull red heat, even when aided by high pressure, not more than traces of ammonia were produced when nitrogen and hydrogen were brought together in the ratio to form ammonia. Two distinctive features

- J. S. C. I. 1906, **25**, 365; 1912, **31**, 280, 283, 851; 1913, **32**, 230; 1914, **33**, 590; 1915, **34**, 125; 1917, **36**, 777. Chem. Eng. 1915, 337. Elect. Rev. 1911, **69**, 531. Proc. of Amer. Inst. Elect. Eng. 1915, 337. Sci. Amer. Suppl. 1913, 126; 1915, Sept. 25th. Smithsonian Institution Report, 1913, 359. Chem. Trade J. & Chem. Eng. 1909, **44**, 621; 1915, **51**, 60, 68, 155, 179, 285, 288; 1915, **56**, 5, 553; 1915, **57**, 26. Met. Chem. Eng. 1906, 137; 1913, 438, 476, 711; 1915, 213, 218, 241, 314, 325, 620; 1916, 418, 425, 513. Metall und Erz. 1916, **13**, 21. Trans. Amer. Elect. Soc. 1909. Iron & Coal Trades Review, 1913, May 23rd. Dingl. Poly. 1875, **218**, 219. Compare Can. P. 164857, 164858, 166832, 166880, 166881, 166882, 173157, 173158, 173159.
1. F. Haber, Zts. Elektrochem. 1903, **9**, 381; 1907, **13**, 460; 1910, **16**, 244. Zts. ang. Chem. 1914, **27**, 1, 473. J. S. C. I. 1914, **33**, 51. Chem. Ztg. 1911, **38**, 695; 1915, **39**, 24; abst. J. S. C. I. 1914, **33**, 871; 1915, **34**, 278. Deut. Physik. Ges. Nov. 6, 1915; Chem. Ztg. 1915, **39**, 24; J. S. C. I. 1915, **34**, 278. F. Haber and J. Coates, Zts. physik. Chem. 1909, **69**, 337. F. Haber and H. Greenwood, Zts. Elektrochem. 1915, **21**, 241; J. S. C. I. 1915, **108**, ii, 443; J. S. C. I. 1915, **34**, 902. F. Haber and A. Koenig, U. S. P. 938316. E. P. 15490, 1908; F. P. 392670; Mon. Sci. 1909, **71**, 133; 1911, **75**, 569, 571; Jahr. Chem. 1909, **62**, 1, 529; Chem. Ztg. Rep. 1909, **33**, 10; J. S. C. I. 1909, **28**, 28. Zts. Elektrochem. 1907, **13**, 723; J. S. C. I. 1907, **26**, 27. Zts. Elektrochem. 1908, **14**, 689; J. S. C. I. 1908, **27**, 1070. F. Haber, A. Koenig, E. Platou and W. Holwech, Zts. Elektrochem. 1910, **16**, 789. Ber. 1907, **40**, 2444; Zts. Electrochem. 1908, **14**, 181, 513; 1913, **19**, 53; J. S. C. I. 1913, **32**, 134; Met. and Chem. Eng. 1913, **11**, 211; J. Ind. Eng. Chem. 1913, **5**, 328. F. Haber and A. Maschke, Zts. Elektrochem. 1915, **21**, 128; J. S. C. I. 1915, **34**, 1089. F. Haber and G. Van Oordt, Zts. anorg. Chem. 1905, **43**, 111; 1905, **44**, 341. F. Haber and S. Tamaru, Zts. Elektrochem. 1915, **21**, 191. F. Haber, S. Tamaru and C. Pommaz, Zts. Elektrochem. 1915, **21**, 89.
- The Haber plant at Oppau, Germany, has been inspected and reported upon in detail by: R. McConnell, J. S. C. I. 1919, **38**, 351-R. W. Bannard, Sugar, 1918, **20**, 271. R. Davis and H. Bryan, Amer. Fertilizer, 1917, **47**, 29; C. A. 1918, **12**, 1911. E. Worden, Fertilizer and Feeding-stuffs J. 1919, **1**, 47; Drug and Chemical Markets, 1919, **5**, 23; Chem. Age, 1919, **1**, 275; Perf. and Essent. Oil Rec. 1919, **10**, 236. P. Drinker, Chem. Age, 1919, **1**, 299. Compare also in this connection, R. Skerrett, Iron Age, 1916, **97**, 359. Nature, 1916, **96**, 537. Chem. Ztg. 1914, **38**, 593; abst. J. S. C. I. 1914, **33**, 590; J. S. C. I. 1914, **6**, 597. Rollason, E. P. Appl. 8614, 1918; J. S. C. I. 1918, **37**, 325-A. A. Bambach, F. P. 469331; abst. J. S. C. I. 1905, **34**, 79. M. Taliani, U. S. P. 1270989, 1918; abst. J. S. C. I. 1918, **37**, 580-A. W. Holwech, Zts. ang. Chem. 1908, **21**, 2131; abst. J. S. C. I. 1908, **27**, 1057; Zts. Elektrochem. 1910, **16**, 369. W. Holwech and F. Koenig, Zts. Electrochem. 1910, **16**, 803. F. Russ, Zts. ang. Chem. 1912, **25**, 586; abst. J. S. C. I. 1912, **31**, 383. V. Ehrlich and F. Russ, Monatsh. Chem. 1911, **32**, 917; abst. J. S. C. I. 1911, **30**, 1264. For exhaustive résumé of the Haber process, see the 5730 page report No. 13228 of 1918 made to the U. S. Bureau of Aircraft Production by E. Worden, P. Drinker, J. Buford, L. Rutstein and R. Dort.

characterize the manufacturing process, i. e., the necessity of maintaining the mixture of gases under a pressure of from 175 to 200 atmospheres, and that the reaction occurs best in the presence of uranium as the catalytic agent.¹

The operation and the requisite plant are by no means complicated. The mixture of one volume of nitrogen to three volumes of hydrogen—corresponding to the formula of ammonia, NH_3 —is forced under a pressure of at least 175 atmospheres into a steel cylinder, where the temperature is maintained at 500° , and in which there is a certain amount of powdered uranium. In the presence of this metal, which remains unchanged and exerts its catalytic power for an indefinite time, the two gases combine to form ammonia, under the given conditions of pressure and temperature. The reaction is rapid at first but decreases steadily in intensity. When ammonia gas forms about 8% of the contents of the cylinder, the reaction has become so slow that the product must be removed. This can be effected by allowing the contents of the cylinder to pass into a vessel, in which the gases may be cooled down to the point at which ammonia is liquefied, in which form it is easily withdrawn by a tap from the apparatus. The ammonia may likewise be withdrawn by bringing these sufficiently cooled gases in contact with such an acid absorbent as sulfuric acid. In either case the residual uncombined mixture of nitrogen and hydrogen is forced back by a pump into the reaction chamber.

The plant consists, therefore, of a reaction cylinder, a cooling chamber and a force pump. The latter keeps the supply in the reaction cylinder constant under a fixed pressure. There is a continuous circulation back and forth between the cylinder and the cooling chamber. From the latter ammonia is withdrawn at regular intervals in the liquid or gaseous form or after absorption as an ammonium salt in solution.

The catalytic agent employed is the most interesting feature in the process, as in the analogous industrial method of manufacturing sulfur trioxide by the aid of platinum sponge. Osmium, a member of the platinum group of metals, was also found to be the most effective agent in bringing about the combination of nitrogen

1. Data in this topic has been taken from "The Nitrogen Problem," Norton.

and hydrogen. The available supply of osmium is, however, extremely limited, the entire amount in the earth's crust being estimated by A. von Welsbach at between 200 and 300 pounds.

Further experiment has shown that the more common metal uranium is nearly as effective as osmium, and it has been adopted as the most practical and serviceable material for the purpose. The product containing uranium carbide, secured from the action of carbon on uranium oxide in the electric furnace, is an especially convenient form. When brought in contact with the mixture of nitrogen and hydrogen under pressure it absorbs nitrogen and falls into an extremely fine powder, which possesses the catalytic property in a high degree.

In a later patent (D. R. P. 238450) the inventor states that yields of over 2% can be secured when so inexpensive a catalytic agent as iron is employed, provided the pressure be increased so as to range from 200 to 250 atmospheres.

The Haber process has come under control of the Badische Co., who have perfected it in many essential respects. They have found that when iron is used as a catalyst its activity may be enhanced by the presence of other elements of the iron group. Molybdenum and molybdic acid have also been found valuable as catalysts, after first being heated in a current of ammonia and changed into nitride. For the purpose of protecting the walls of the reaction chamber from disintegration the catalyst is contained in an inner tube or vessel, the mixture of gases entering the outer space between the external walls of the reaction chamber and the tube, then passes into the latter, and finally is conducted directly into the chamber for separating the resultant ammonia. Undoubtedly many further perfections in process and apparatus will be recorded in the form of patents during the next few years.

Three essential items in the cost of producing ammonia by this synthetic method are plant, material and fuel. The plant for such an industrial process will of necessity be somewhat of a novelty in technical construction. Hitherto chemical operations on a large scale were carried out under a pressure of 200 atmospheres have been unknown. The rapidly growing industry of liquefied gases has shown that there are no great difficulties in the way of constructing the requisite plant. Reaction chambers must necessarily possess a narrow diameter. Steel flasks of

2.75 inches inner diameter, with walls 0.2 inch thick used in this synthesis easily sustain a pressure of 200 atmospheres. The inert nature of the two gases employed and the chemical properties of the product render it easy to prevent deterioration by corrosion and insures a comparatively long life for the more massive forms of apparatus and probably also for connections, taps and other minor accessories. Pumping outfits adequate for effective work in this process are already in use for liquefying air and other gases, and for compressing gases for transportation. Hydrogen and oxygen usually are sent in steel flasks under a pressure of 150 atmospheres.

With regard to consumption of material there probably will be a small item of expense in connection with the deterioration of the catalytic substances as in other contact processes, probably less than in the manufacture of sulfuric acid.

Badische Process for Synthetic Ammonia Formation. The Haber processes previously described have been absorbed by the Badische Anilin und Soda Fabrik,¹ who have amplified and perfected the methods in many basic ways. Especially has progress been made by them in the selection of proper catalysts. They have found that ammonia² formed by the union of nitrogen and hydrogen in the presence of a catalytic agent is condensed by abstracting heat from a surface in, or forming part of, the vessel in which the combination has taken place. A suitable arrangement of apparatus is shown in Fig. S2, in which the reaction vessel A, capable of withstanding pressure, is surrounded by a cooling jacket B. The catalytic material, for example, uranium nitride, is contained in a vessel D, open at both ends and suspended

1. E. P. 14023, 1910; abst. J. S. C. I. 1910, **29**, 1453; Chem. Ztg. Rep. 1911, **35**, 3. F. P. 406969; abst. Mon. Sci. 1910, **73**, 175; Chem. Ztg. Rep. 1910, **34**, 126. Swiss P. 72690, 1916, addn. to Swiss P. 69951; abst. C. A. 1916, **10**, 2621. Holl. P. 2065, 1917; abst. C. A. 1917, **11**, 2720. U. S. P. 1053951, 1053952, 1913; E. P. 28167, 1911; 9841, 9842, 1912; F. P. 425099, addn. 16622; D. R. P. 246377, 247852, 249447, 256855, 258146; D. R. P. Ann. B. 65369, 65690; Aust. P. 4132, 8979, 1912; 58408; abst. Chem. Ztg. 1913, **37**, 152, 163, 228, 254, 302, 336, 397. See also M. Berthelot, Bull. Soc. Chim. 1874, **21**, 100; J. C. S. 1874, **27**, 439, 440, 868, 1057; J. pharm. chim. 1874, **19**, 97, 182; Ber. 1874, **7**, 188; Jahr. Chem. 1874, **27**, 112, 220, 221. F. Raschig, abst. Zts. ang. Chem. 1905, **18**, 1281; J. C. S. 1905, **88**, ii, 23, 700; J. S. C. I. 1905, **24**, 923; Chem. Centr. 1905, **76**, II, 932. Centralstelle f. Wissenschaftlich-Technische Untersuchungen, Belg. P. 259926; Aust. P. 9206, 1912; F. P. 450465; abst. Chem. Ztg. 1913, **37**, 228, 244, 316.
2. E. P. 13097, 1910; abst. J. S. C. I. 1911, **30**, 748. Badische Co., Belg. P. 226135, 227342, 1910; 257401, 257897, 1913. F. P. 418434.

in the vessel A. The catalytic material is heated by the electric resistance coil E, which is provided with a protective covering G, around which the gases are caused to circulate.

Better yields are said to be obtained¹ by the addition of substances termed "promoters" to the iron, nickel or cobalt used as the catalytic agent. These substances are generally compounds of magnesium, beryllium, aluminium or of the alkali, alkaline-earth, or rare-earth metals, or of zirconium, vanadium, tantalum, chromium, manganese, molybdenum or tungsten. The addition of the oxide or other compound of magnesium or aluminium is particularly favorable. It is found, however, that certain bodies have the property of diminishing or destroying the catalytic property of the iron, etc. Such bodies are, for example, arsenic, sulfur, selenium tellurium, phosphorus, boron, antimony, bismuth, tin, lead or zinc, or their compounds, and the presence of carbon monoxide and dioxide, and of oil in the gases should be avoided. Iron, etc., which is unsuitable for use as a catalyst owing to the presence of contact poison or for other reasons, can be rendered effective by heating to a high temperature in admixture with a promoter,

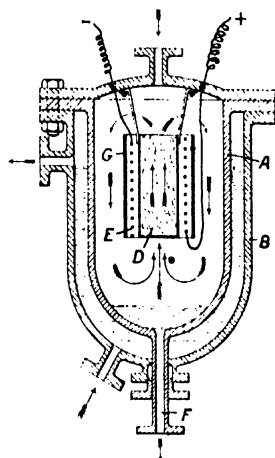


FIG. 82.—THE BADISCHE SYNTHETIC AMMONIA APPARATUS

- so that a mixture of oxides is obtained, which is reduced by means of hydrogen, preferably at as low a temperature as possible. It is preferred that the first heating should be sufficient to melt the mixture. This treatment may be repeated until the desired result is obtained. The reaction gases may be freed from contact poison by passing over a material capable of absorbing it, and this material may be a further quantity of the catalytic agent placed in advance. The mixture of iron and a promoter may be supported on a carrier, such as

¹ E. P. 19249, 19250, 19251, 1910. See also E. P. 14023, 1910; abst. C. A. 1912, **6**, 1346; J. S. C. I. 1910, **29**, 1453; 1911, **30**, 1116; Chem. Ztg. Rep. 1911, **35**, 575. Belg. P. 219271, 1909; 230732, 1910; 235631, 238913, 1911; 244126, 246208, 1912. Swiss P. 43630, 1908; 50538, 51899, 1910.

asbestos or chamotte, and one constituent of the carrier may constitute the promoter, but it is necessary in this case that the iron and promoter should be actually mixed together. In use, a mixture of nitrogen and hydrogen, preferably in combining proportions, is passed over the heated catalytic agent.

By the union of nitrogen and hydrogen under pressure and in the presence of a catalytic agent,¹ it has been found that the walls of the steel or other containing vessels may be heated directly either by the external heat or by heating the vessel internally, for instance, by preheating the entire gases or by a combination of these methods. The vessel is heated to a temperature approaching that at which the reaction takes place and the heating may be effected, for example, in a bath of molten saltpeter. The vessel may be given interior and exterior coating of protective material such as enamel.

They have found that catalysts consisting of metals of the iron group may be² freed from contact poison, and a mixture of nitrogen and hydrogen is passed into the catalyst at a raised temperature, while excluding contact poison. Catalysts which can be so treated and rendered suitable for use in the production of ammonia are iron, nickel, tungsten, molybdenum and uranium. The most convenient method of removing contact poison is to oxidize the iron at a high temperature and subsequently to reduce the oxide to metal. This treatment is repeated until no further increase in catalytic power is obtained. For the continued activity of the catalytic agent, the gases should be freed from bodies which act as contact poisons; and these latter can be removed by passage over a substance which absorbs them, for example, an additional mass of the catalytic agent. In examples, iron is melted in a current of oxygen, and the resulting oxide is broken into small pieces and reduced by means of hydrogen at as low a temperature as possible; magnetite is subjected to oxidation and reduction several times. If desired, the catalytic agent can be further improved by the addition of a promoter.

Better yields³ of ammonia are obtained in the synthetic

1. E. P. 15973, 1910. See also E. P. 14023, 1910; abst. J. S. C. I. 1910, **29**, 1453; 1911, **30**, 957.

2. E. P. 19778, 1910. See also E. P. 19249, 1910; abst. J. S. C. I. 1911, **30**, 1116, 1253; C. A. 1912, **6**, 1346, 1503; Chem. Ztg. Rep. 1911, **35**, 575.

3. E. P. 5835, 1911; abst. C. A. 1912, **6**, 2500; J. S. C. I. 1911, **30**, 1115; Chem. Ztg. Rep. 1911, **35**, 575. Compare E. P. 483618. D. R. P.

process if a promoter is added to the catalyst other than iron, cobalt and nickel, while excluding contact poisons. Oxides or other suitable compounds of the alkali and alkaline-earth metals, earth metals, the rare-earth metals, and also tantalum and niobium are suitable as promoters, while contact poisons include the metalloids such as sulfur, selenium, tellurium, arsenic, phosphorus, and also the easily fusible metals.

They have patented¹ as catalysts for use in the synthetic production of ammonia a mixture of iron or cobalt, and a promoter, free from active contact poison. The addition of a promoter has the effect of increasing the yield of ammonia, and the bodies added are generally compounds of elements such as magnesium, beryllium, aluminium, the rare-earth metals, uranium, thorium, zirconium, vanadium, niobium, tantalum, chromium, manganese, molybdenum and tungsten. The addition of the oxide or other compounds of magnesium or aluminium is particularly favorable. The bodies that act as contact poisons are, for example, sulfur, selenium, tellurium, phosphorus, boron, antimony, lead, bismuth, tin and zinc and their compounds, and carbon monoxide and some other carbon compounds. Contact poison may be removed by heating the mixture of the promoter and iron, etc., or a suitable compound in such a manner that a mixture of oxides is obtained, and then reducing this in hydrogen. The heating should preferably be effected so that the mixture melts, and the reduction should be effected at as low a temperature as possible. The treatment is repeated if necessary. The gases should be freed from contact poison such as arsenic, sulfur and oil, by passage over a material capable of absorbing it, and this material may be a further quantity of catalytic material arranged in advance. The mixture of iron and a promoter may be supported on a carrier such as chamotte or asbestos, and a constituent of the carrier may constitute the promoter, but it is necessary in this case that the iron and promoter should be actually mixed.

The synthesis of ammonia may also be advantageously

238340; abst. C. A. 1912, **6**, 1575; Chem. Zentr. 1911, **82**, II, 1077; Chem. Ztg. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 505; Zts. ang. Chem. 1911, **24**, 2029.

¹ E. P. 5833, 5834, 5836, 1910; abst. C. A. 1912, **6**, 2500; J. S. C. I. 1911, **30**, 1115.

effected¹ by employing as the catalyst chemically pure iron or a nitride of chemically pure iron, which has been prepared from a compound at a temperature not materially exceeding 600°. The catalyst so obtained is used at a comparatively low temperature, preferably a temperature not exceeding 600°. A particularly active form of iron is obtained, if the oxide to be reduced has been prepared by heating iron or iron oxide to a high temperature, preferably until the resulting iron oxide melts. The oxidation and reduction may be repeated, and it is only necessary to maintain a low temperature during the final reduction.

Ammonia may also be obtained from nitrogen and hydrogen² by the use of a catalyst comprizing a metal or metallic compound capable of absorbing nitrogen and a metal or metallic compound capable of absorbing hydrogen, other promoters being added if desired; in an example, palladium and molybdenum are employed with, if desired, an addition of uranium. The metallic compounds that may be used are the products of the action of hydrogen or nitrogen on the metal or compounds which, under the conditions of treatment, yield such bodies, for instance, uranium and cerium carbides.

They assert that³ deterioration of the manganese used as the catalyst in the synthetic production of ammonia is prevented by the use of a mixture of nitrogen and hydrogen which has been freed from all traces of oxygen, whether free or combined. The gases may be so freed by passage over metallic sodium, or manganese nitride or other substances that will decompose water and fix oxygen, and they may be subjected to a preliminary treatment by passage over heated palladium asbestos and calcium chloride. The same precautions must be taken if manganese nitride is used

1. E. P. 24657, 1911; abst. C. A. 1913, **7**, 404; J. S. C. I. 1912, **31**, 817; Chem. Ztg. Rep. 1912, **36**, 581. See A. Brochet and G. Boiteau, E. P. 425952; abst. J. S. C. I. 1911, **30**, 1012; C. A. 1912, **6**, 1969; Mon. Sci. 1913, **79**, 121; Chem. Ztg. Rep. 1911, **35**, 507.

2. E. P. 21151, 1911; abst. C. A. 1913, **7**, 1083; J. S. C. I. 1912, **31**, 1031. See also E. P. 10441, 19259, 1910; abst. J. S. C. I. 1911, **30**, 87, 1116; C. A. 1912, **6**, 1346; Chem. Ztg. Rep. 1911, **35**, 575. E. P. 61, 5833, 5835, 17411, 1911; abst. J. S. C. I. 1911, **30**, 1057, 1115; 1912, **31**, 282; C. A. 1912, **6**, 2500; 1913, **7**, 403; Chem. Ztg. Rep. 1911, **35**, 575; J. Soc. Dyers Col. 1911, **27**, 241. H. Cohn and E. Geisenberger, Swiss P. 19895, 1899.

3. E. P. 26749, 1911; see also E. P. 19778, 1910; 5835, 1911; abst. C. A. 1912, **6**, 1503, 2500; 1913, **7**, 1789; J. S. C. I. 1911, **30**, 1115, 1253; 1912, **31**, 385.

as the catalyst. Other nitrides have proven equally efficient.

The ammonia¹ that has been prepared catalytically is freed from nitrogen and hydrogen by fractional distillation of the liquefied ammonia, preferably under pressure. A distilling apparatus provided with a dephlegmator and condenser may be employed, or the liquid ammonia may be allowed to flow down a fractionating column, the nitrogen and hydrogen being carried off at the top, while pure ammonia is led to a condenser from a lower point. The escaping portion, containing the nitrogen and hydrogen, is washed to recover the ammonia.

In another method² ammonia is prepared by passing nitrogen and hydrogen alternately over an agent containing two or more metals, or compounds which during the reaction give rise to metals, and capable of taking up nitrogen or hydrogen or both. One or more of the metals may be replaced by its nitrogen or hydrogen compound, or by a body which during the reaction gives rise to such compound, and a body which will promote the reaction may be added to the mixture. In an example, the mixture used is lithium-manganese.

The production of ammonia as described in the parent English specification may be³ modified by passing nitrogen and hydrogen alternately over heated molybdenum, or a nitrogen compound. Increased pressure is preferably used in the process, especially during the passage of the nitrogen, and the temperature is generally kept below 600°. The nitrogen used may contain a small quantity of hydrogen, and other suitable compounds may be added to the molybdenum. In an example, molybdenum nitride, prepared by treating molybdic acid or molybdenum chloride with ammonia, is used.

The gases⁴ after they have been purified are allowed only to come in contact with apparatus formed of nickel or nickel alloys, or other compounds which do not yield dust-like particles to the gases. Gases are purified and are prevented from acquiring dust-

1. E. P. 25259, 1912; abst. C. A. 1914, **8**, 407; J. S. C. I. 1913, **32**, 909; Chem. Ztg. Rep. 1913, **37**, 634.

2. E. P. 3345, 1912. See also E. P. 19249, 1910; 5833, 5835, 21151, 28167, 1911; abst. C. A. 1912, **6**, 1346, 2500; 1913, **7**, 1083, 1958, 2668; J. S. C. I. 1911, **30**, 1115, 1116; 1912, **31**, 1031; 1913, **32**, 85; Chem. Ztg. Rep. 1911, **35**, 575.

3. E. P. 9842, 1912; abst. C. A. 1913, **7**, 2838; J. S. C. I. 1913, **32**, 289.

4. E. P. 9263, 1913; abst. C. A. 1914, **8**, 3355; J. S. C. I. 1914, **33**, 593.

like impurities in their passage to the catalytic agent. The carrying of dust-like impurities is prevented by keeping the gases from coming in contact with iron or copper, or other material of the apparatus which yields dust-like impurities to the gases.

In a later process for the manufacture of nitrogen oxides by the catalytic oxidation of ammonia¹ with air or oxygen with employment of metals of the ferric group or their oxides as catalyzers, the addition of bismuth or its compounds materially increase the catalytic activity of the specified agents. Binding agents may be added also, but metalloid compounds are to be avoided. The contact masses are best employed in the form of a layer of separate pieces, that is, a mixture of 45 parts of pure iron or manganese nitrate and one-half part of bismuth nitrate is dissolved with the addition of pure nitric acid. The precipitation is effected with ammonia, the precipitate dried to some extent, formed into dice-shaped pieces, carefully heated and then charged into a tube through which ammonia and air are led. At about 700° a yield of over 90% of nitrogen oxide is obtained. Such a contact mass can be made also by the oxidizing melting of a mixture of pure iron powder and with 3% bismuth trioxide and subsequent grinding. Metallic iron itself may be activated with bismuth or its compounds and then introduced into the contact furnace. This company² treats the conduits and apparatus for carrying gases containing ammonia to the catalyzers, if they consist of material liable to give up dusty impurities to the gases, by a purifying process, or brings the previously purified gases before entering into the catalyzing apparatus into contact only with such metals which do not, like iron and copper, give up dusty impurities to the gases, thus quickly impairing the contact action of platinum. Nickel or alloys containing much of it are suitable for this purpose.

According to Uhde³ the recent development of the synthesis

1. D. R. P. 283824, 1914; abst. C. A. 1915, **9**, 2577. See also C. A. 1915, **9**, 1673; Chem. Zentr. 1915, **86**, I, 1031; Chem. Ztg. Rep. 1915; **39**, 186; Zts. ang. Chem. 1915, **28**, 295.

2. U. S. P. 1091689, 1094182; abst. C. A. 1914, **8**, 1857, 2039; Mon. Sci. 1914, **81**, 100, 137; Chem. Ztg. Rep. 1914, **38**, 378; Zts. ang. Chem. 1915, **28**, I, 177. E. P. 9263, 1913; F. P. 464237, 464285; abst. Mon. Sci. 1915, **83**, 57; 1916, **84**, 11; Chem. Ztg. Rep. 1914, **38**, 571; C. A. 1914, **8**, 3355; J. S. C. I. 1914, **33**, 549, 593. D. R. P. 280499; abst. Chem. Zentr. 1915, **86**, I, 70; Chem. Ztg. Rep. 1914, **38**, 586; Wag. Jahr. 1914, **60**, I, 353; Zts. ang. Chem. 1915, **28**, 20.

3. Chem. Ztg. 1914, **38**, 1015. Consult M. Taliani, U. S. P. 1270989,

of ammonia by the method of Haber and the Badische Anilin- und Sodafabrik, is the best foundation for an economical conversion of ammoniacal nitrogen into nitric acid, because the ammonia can be employed without purification, and the cost of plant and working is not excessively large.

The Ostwald Process.¹ The problem of the oxidation of ammonia to nitric acid has engaged the attention of scientists for many years, and was finally solved as a commercial proposition by W. Ostwald in 1902, aided by E. Brauer. The process is protected by patents,² but a patent could not be obtained in his 1918; abst. 1918, **12**, 1913; J. S. C. I. 1918, **37**, 580-A. E. P. Appl. 5979, 1918; J. S. C. I. 1918, **37**, 227-A. C. Bosch, U. S. P. 1261900; abst. C. A. 1918, **12**, 1588; J. S. C. I. 1918, **37**, 303-A. In this connection see F. Brunck, Belg. P. 180406, 1904; 186030, 1905.

1. The Ostwald process was first put into commercial operation at Gerthe, Westphalia, in 1909, and later at Vilvorde, Belgium. During the war plants using this process were operated at Augouleme, France, and Dagenham, England. The following is the résumé of the 1917 report of D. Paschal on the operation of the Augouleme plant:

(1) The storage does not give rise to a loss of nitrogen but to an increase in the dead weight.

(2) The operation of the autoclaves, notwithstanding the appearances, seems to be that part of the manufacture the least known in its details and perhaps the most difficult to manage; it is, moreover, influenced, doubtless, by the anterior transformations of the cyanamide.

(3) The catalyzers give an actual yield of about 90% and we think a means may be devised to make this figure rise from 94% to 96%.

It is important to notice that this gain will be acquired at the price of a diminution exactly equivalent to the rate of ammonia in the gas in such a way that the hourly yield of the installation will not be affected either for good or bad.

(4) In winter the towers give an average absorption of 97%, which may be conserved in summer with proper refrigeration. The yield was found to be: $96 \times 0.90 \times 0.97 = 83.8\%$.

2. E. P. 698, 8300, 1902; 7909, 1908; J. S. C. I. 1902, **21**, 548; 1903, **22**, 420; 1908, **27**, 898; C. A. 1909, **3**, 696; Chem. Ztg. 1903, **27**, 457. U. S. P. 858904, 1907; abst. C. A. 1907, **1**, 2483, 2758; Mon. Sci. 1908, **69**, 20; Chem. Ztg. Rep. 1907, **31**, 408. D. R. P. 207154, 1906; abst. J. S. C. I. 1909, **28**, 365; C. A. 1909, **3**, 1919; Chem. Zentr. 1909, **80**, 1, 1127; Chem. Ztg. Rep. 1909, **33**, 145; Jahr. Chem. 1909, **62**, 531; Wag. Jahr. 1909, **55**, 1, 415; Zts. Schiess. Spreng. 1909, **4**, 108. F. P. 317544; addn. dated April 9, 1902, to F. P. 317544; 389059. Abst. Mon. Sci. 1903, **59**, 120. Swiss P. 25881. See also Chem. Ztg. 1903, 457; Berg. u. Hüttenm. Ztg. 1906, **3**, 71; J. S. C. I. Ann. Rept. 1916, **1**, 28. D. R. P. 168272; abst. Chem. Centr. 1906, **77**, 1, 1198; Chem. Ztg. 1906, **30**, 425; Chem. Zts. 1906, **5**, 344; Jahr. Chem. 1905-1908, I, 1777; Wag. Jahr. 1906, **52**, 1, 449; Zts. ang. Chem. 1906, **19**, 1941; Zts. Schiess. Spreng. 1906, **1**, 103. D. R. P. 224329; abst. Chem. Zentr. 1910, **81**, II, 511; Chem. Ztg. Rep. 1910, **34**, 397; Jahr. Chem. 1910, **63**, 1, 587; Wag. Jahr. 1910, **56**, 1, 485; Zts. ang. Chem. 1910, **23**, 2098; Zts. Schiess. Spreng. 1910, **5**, 338. Aust. P. 42407. Belg. P. 148862, 1900; 162590, 1902; 207221, 1908. W. Ostwald and E. Brauer, Compt. rend. 1905, **141**, 861; 1906, **142**, 430, 1239. O. Schmidt and R. Böcker, Ber. 1906, **39**, 1866. G. Schüpphaus, Metall. u. Erz. 1916, **13**, 21; J. S. C. I. 1916, **35**, 613; Met. and Chem. Engng. 1916, **14**, 425.

own country because of prior publication of the basic features of his invention, many years before.

As far back as 1839 F. Kuhlmann¹ observed that when mixtures of air and ammonia were simultaneously conducted through tubes containing platinum sponge or nickel or copper in a finely divided condition, the temperature meanwhile being kept slightly above 300°, nitric and nitrous acids were obtained. H. Warren in 1891² succeeded in obtaining ammonium nitrite when ammonia and oxygen were passed over platinized asbestos at a dull red heat. R. Marston in 1900³ obtained nitric acid by passing the gaseous mixtures over hot copper and similar contact materials. Other chemists have observed the facility with which ammonia undergoes oxidation when in contact with ozone. The readiness with which bacterial organisms in the soil attack ammonia and oxidize it to nitrous and nitric acids is well known.

Ostwald very exhaustively investigated the conditions most favorable for the reaction, and combined them in such a manner as to constitute a successful invention. The members of the platinum group of metals were found to be the most efficient catalytic agents, together with the higher oxides of manganese, lead, copper, silver, iron, cobalt and nickel. Best results were obtained by the use of a compact sheet of platinum with a roughened surface partly coated with spongy platinum or platinum black; being the same physical condition as is produced when a smooth sheet has been used for some time for this purpose. While it was found that platinum sponge gave the best yield in the sulfuric acid contact method, it induces a too rapid reaction in the case of nitric acid, so that a less energetic catalyst is preferable.

Ostwald found that a mixture of ammonia and an excess of air is converted catalytically into nitric acid or higher nitrogen oxides by passing over solid or spongy platinum, or a compound of the two, or over metallic iridium, rhodium or palladium, or over oxides of heavy metals, such as lead, or over silver, copper, iron, chromium, nickel, or copper oxide. The catalytic material

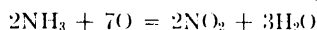
1. Ann. 1839, **29**, 281; Mem. Soc. Sci. Lille, 1838, 88; abst. Berz. Jahr. 1840, **19**, 178.

2. Chem. News, 1891, **63**, 294; abst. J. C. S. 1891, **60**, 1321. See L. Devaucelle, Belg. P. 232622, 1911. F. Daub, Belg. P. 149301, 1900. Elektrochemische Werke Ges., Belg. P. 233388, 1911.

3. E. P. 19074, 1900; abst. Chem. Ztg. 1902, **26**, 206; J. S. C. I. 1901, **20**, 1209; Mon. Sci. 1902, **58**, 154.

is in every case heated to a red heat. Free nitrogen is also liberated, but its quantity is kept as low as possible. In one form platinum foil is arranged in alternate series of flat and corrugated strips, the gases passing through the tubular passages formed thereby; but the foil may be otherwise twisted or made uneven. In other arrangements several layers of wire netting or of perforated plates may be used, or a resistant material, such as porcelain, may be coated with platinum, or, finally, shavings, chips, balls of wire, or the like, may be used as porous layers or bungs. The mixture of air and ammonia may be formed by passing air in contact with a solution containing ammonia, the air flowing in the reverse direction to the ammoniacal solution. The ammoniacal solution may be heated, the heat generated by the catalytic reaction being conveniently employed for this purpose. In a later patent,¹ improvements in the catalysts employed were made as follows:

(1) The proportion of oxygen to ammonia should preferably be in excess of that required by the following equation:



(2) The oxygen is preferably used in the form of air.

(3) The temperature of the reaction should exceed 300° , a temperature between a dark and bright red heat being suitable.

The catalytic apparatus for the transformation of ammonia into nitric acid is comparatively simple and consists of one or more bodies which fill the cross-section of the reaction chamber and are built up of parallel or approximately parallel strips of catalytic material with suitable interspaces, the strips being inclined to the direction of the flow of the gases. The plates of one body may be inclined at an angle different from the plates of the preceding body, and the several bodies may be partly rotated, spaces being left between the rotating bodies.²

The actual working of the apparatus is as follows:³ The mixture of air and ammonia obtained by sucking air through the ammonia water of gas works, to which lime has been added, enters at one extremity of a wide tube. It finds its exit through a narrower tube, open at the other extremity of the wider inclosing

1. E. P. 8300, 1902; abst. J. S. C. I. 1903, **22**, 420.

2. E. P. 7909, 1908; abst. C. A. 1909, **3**, 696; J. S. C. I. 1908, **27**, 898.

3. As described by T. Norton, "Utilization of Atmospheric Nitrogen," page 42.

tube, extending through the entire length of the latter, in an axial line, and terminating in an absorption chamber. The catalytic material is placed in the inner tube. This arrangement, that of the reverse current, enables the air-ammonia mixture to regulate automatically the temperature of the reaction, and prevent it from becoming too violent. The air current is sucked through ammonia solutions of constantly increasing strength, so as gradually to exhaust them, and the heat of the reaction is transferred to these solutions. The temperature is kept at a dull-red heat.

The construction is thus comparatively simple. The controlling factor is the rapidity of the gas current, which must be so regulated as to avoid, on the one hand, too long contact with the catalytic substance and a consequent formation of nitrogen and water, and on the other, an insufficient opportunity for nearly all of the ammonia present to participate in the reaction. Thus far it has not been possible to oxidize more than 85% of the ammonia to nitrous and nitric oxides. Ostwald has found it advantageous to regulate the operation so that only one-half of the ammonia should be converted into nitric acid, and that this should combine with the remaining half to form ammonium nitrate, NH_4NO_3 . This salt is admirably adapted for use as a fertilizer. It contains 35% N (ammonium sulfate, 20% to 21%; Chile saltpeter, 15.5%), and hence there is a notable economy involved in its transportation. Further, no sulfuric acid is needed for its manufacture. It is hygroscopic, and must be protected from exposure to air. At present it is employed for a variety of minor chemical operations, such as the preparation of laughing gas. The chief demand, however, is for use in the manufacture of safety explosives. In this form, for the time being, there is a large field for the extension of the Ostwald process. If it is found most economical to limit the contact process to the production of this salt, it is not difficult to regenerate the ammonia present by treatment with lime, and from the resultant calcium nitrate to liberate the nitric acid by treatment with sulfuric acid.

According to G. Schüpphaus,¹ nitric acid may be produced from ammonia by the Ostwald process when ammonia liquor is mixed with milk of lime, and the liquid treated with steam in a

1. Metall. and Erz, 1916, **13**, 21; Met. and Chem. Eng. 1916, **14**, 425; J. S. C. I. 1916, **35**, 631; abstr. C. A. 1916, **10**, 1580.

separating column, the gas being cooled to condense the steam and the ammonia afterwards washed in caustic soda solution of 30° B. (1.26 sp. gr.). If ammonium chloride solution is used the purification of the gas may be omitted. The ammonia gas is thoroughly mixed with a suitable quantity of air, and the mixture passed over a platinum gauze catalyst heated to about 700°, thus forming nitric oxide and water. The lower half of the casing surrounding the gauze is cooled by water to prevent, as far as possible, decomposition of the ammonia before it reaches the catalyst. The nitric oxide is led off through a conical iron hood lined with aluminium, and an aluminium elbow to a sulfuric acid plant, an iron plate trap being provided to prevent the possible passage of chamber gases back to the platinum catalyst.

From a résumé of the available information (which is to be regarded with reserve), F. Zeisberg¹ concludes that the Ostwald and similar processes for the manufacture of nitric acid by the catalytic oxidation of ammonia can hardly compete with the sodium nitrate or arc process, the possible margin of profit being very small even when the price of ammonia is low. The process possesses the advantages of being continuous and capable of installation in small units; it also requires little power and relatively small absorption apparatus, the exit gases from the converters being several times as concentrated as those from any arc furnace. It is, however, only a step, not a complete process, and the plant would have to be located with respect to economy of freight on incoming supplies of ammonia liquor or cyanamide, and the cost of ammonia would have to be improbably low for profitable operation.

Catalysts. The success of the ammonia process for nitric acid formation has been developed primarily from the selection and utilization of suitable catalytic bodies. W. Ostwald,² K. Schick,³ J. Eggert,⁴ and O. Dieffenbach and W. Moldenhauer⁵

1. Met. Chem. Eng. 1916, **15**, 299; abst. J. S. C. I. 1916, **35**, 1107; C. A. 1916, **10**, 2966. Compare Belg. P. 156330, 212547, 237870. For production of ammonia by fermentation, see J. Effront, Belg. P. 189218, 1906; 203634, 1907; 209075, 1908.

2. E. P. 698, 1902; abst. J. S. C. I. 1902, **21**, 548; Chem. Ztg. Rep. 1903, **27**, 457. Swiss P. 41262.

3. U. S. P. 971149, 1910; abst. C. A. 1910, **4**, 3286; Mon. Sci. 1913, **79**, 100; Chem. Ztg. Rep. 1910, **34**, 610.

4. Zts. Elektrochem. 1914, **20**, 370; 1915, **21**, 349.

5. U. S. P. 914813, 1909; abst. C. A. 1909, **3**, 1447; Mon. Sci. 1909,

have used platinum alone, while platinum with titanium¹ and the analogous metal ruthenium² have been patented for this purpose.

Nickel in the hands of C. Claessen;³ copper, either alone⁴ or in combination with cupric oxide;⁵ manganese as developed by

71, 139; Chem. Ztg. Rep. 1909, **33**, 219. F. P. 389500; abst. J. S. C. I. 1919, **28**, 365; Mon. Sci. 1909, **71**, 112. E. P. 8768, 1908; abst. J. S. C. I. 1909, **28**, 90. F. Washburn, E. P. 125601, 1916; C. A. 1919, **38**, 2259, uses platinum in the catalytic oxidation of ammonia. Can. P. 173157 8, 1916. D. R. P. 174736; abst. Mon. Sci. 1908, **69**, 153; Chem. Centr. 1906, **77**, 11, 1091; Chem. Ztg. Rep. 1906, **30**, 325; Chem. Zts. 1907, **6**, 19; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1906, **52**, I, 446; Zts. ang. Chem. 1907, **20**, 973; Zts. Schiess. Spreng. 1906, **1**, 343. Swiss P. 43184. H. Adams, J. Partington and E. Rideal (E. P. 135224) employ nickel, iron, chromium or bismuth as catalysts. O. Dieffenbach and C. Uebel, D. R. P. 238370; abst. C. A. 1912, **6**, 1663; Chem. Zentr. 1911, **82**, II, 1078; Chem. Ztg. Rep. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 470; Zts. ang. Chem. 1911, **24**, 2029; Zts. Schiess. Spreng. 1911, **6**, 411. U. S. P. 941768; abst. J. S. C. I. 1910, **29**, 32; 1911, **30**, 1312.

1. Hlavati, F. P. 453207; abst. Mon. Sci. 1914, **81**, 9; C. A. 1914, **8**, 23; Chem. Ztg. Rep. 1913, **37**, 553. Chem. Ind. 1914, **37**, 265; Chem. Ztg. Rep. 1910, **34**, 84. D. R. P. 275343; abst. Chem. Zentr. 1914, **85**, II, 276; Chem. Ztg. Rep. 1914, **38**, 379; Wag. Jahr. 1914, **60**, I, 451; Zts. ang. Chem. 1914, **27**, 431. D. R. P. 275663; abst. Chem. Zentr. 1914, **85**, II, 276; Chem. Ztg. Rep. 1914, **38**, 404; Wag. Jahr. 1914, **60**, I, 451; Zts. ang. Chem. 1914, **27**, 480; J. S. C. I. 1914, **33**, 1009.

2. Badische Anilin und Soda Fabrik, U. S. P. 1173532; abst. J. S. C. I. 1916, **35**, 460. E. P. 12977, 1913; abst. C. A. 1914, **8**, 3842; J. S. C. I. 1914, **33**, 483. E. P. 13848, 1914; abst. J. S. C. I. 1915, **34**, 799. E. P. 7651, 1915; abst. J. S. C. I. 1916, **35**, 1015. E. P. 13297, 1915; abst. J. S. C. I. 1916, **35**, 1108. E. P. 13298, 1915; abst. J. S. C. I. 1916, **35**, 1015. D. R. P. 275518, Zentralstelle für Wissenschaftliche-Technische Untersuchungen Ges.; abst. Chem. Zentr. 1914, **85**, II, 279; Chem. Ztg. Rep. 1914, **38**, 438; Wag. Jahr. 1914, **60**, I, 451; Zts. ang. Chem. 1914, **27**, 471. E. P. 14585, 1912; abst. C. A. 1913, **7**, 4050; J. S. C. I. 1913, **32**, 752. D. R. P. 252997; abst. C. A. 1913, **7**, 541; Chem. Zentr. 1912, **83**, II, 1755; Chem. Ztg. Rep. 1912, **36**, 618; Wag. Jahr. 1912, **58**, I, 386; Zts. ang. Chem. 1912, **25**, 2505. F. P. 450465; abst. J. S. C. I. 1912, **31**, 1178; Mon. Sci. 1914, **81**, 6. Belg. P. 250926, 1912, also uses ruthenium.

3. U. S. P. 1178440; abst. J. S. C. I. 1916, **35**, 633. E. P. 7866, 1914; F. P. 470916; abst. J. S. C. I. 1915, **34**, 176, 834. F. P. 470916; abst. Mon. Sci. 1916, **83**, 66. D. R. P. 289795; abst. J. S. C. I. 1916, **35**, 423; Mon. Sci. 1918, **85**, 20; Chem. Zentr. 1916, **87**, I, 238; Chem. Ztg. Rep. 1916, **40**, 64; Zts. ang. Chem. 1916, **29**, 89. Swed. P. 38645, 41076, 1916; abst. C. A. 1916, **10**, 3140. C. Ellis (U. S. P. 1273772, 1918; 1327029, 1920; abst. J. S. C. I. 1918, **37**, 581-A; C. A. 1918, **12**, 1913; 1920, **14**, 601) employs nickel-cobalt carbide as catalyst.

4. E. Orloff, J. Russ. Phys. Chem. Soc. 1908, 659; abst. C. A. 1909, **3**, 1833; J. C. S. 1908, **94**, ii, 582; Chem. Zentr. 1908, **79**, II, 1500; Jahr. Chem. 1905-1908, I, 1713.

5. Societe le Nitrogene, F. P. 453099; abst. Chem. Ztg. Rep. 1913, **37**, 515. A. de Montlaur, F. P. 445857; abst. J. S. C. I. 1913, **32**, 23; Mon. Sci. 1913, **79**, 143. Belg. P. 256281, 1913. W. Bancroft, Trans. Am. Electrochem. Soc. 1919, **36**; C. A. 1919, **38**, 2795. A. Mailhe, J. usines, gaz. 1919, **43**, 177, 193, 217; abst. C. A. 1919, **13**, 2795. G. Frabetti (E. P. 120551, 1918; abst. C. A. 1919, **13**, 643) advocates the use of platinum-d asbestos, and describes its preparation. For the activation of catalysts and contact masses,

the Badische;¹ tungsten,² nickel and chromium,³ iron and chromium,⁴ cerium and thorium,⁵ ferric oxide,⁶ and the oxides of cobalt, manganese, chromium, nickel and barium have been proposed from time to time⁷ for this purpose. The chlorine or sulfur compounds of lithium or titanium at high temperatures have also been advocated.⁸

Ferro-aluminium,⁹ ferro-silicon,¹⁰ and burnt pyrites,¹¹ as well see E. Maxted and G. Ridsdale, E. P. 127025, 1917; J. S. C. I. 1919, **38**, 535-A. E. Maxted and T. Smith, E. P. 134572, 1918; abst. C. A. 1920, **14**, 803.

1. E. P. 26749, 1911; abst. C. A. 1913, **7**, 1789; J. S. C. I. 1912, **31**, 385; Chem. Ztg. Rep. 1912, **36**, 390. R. De Gregorio (Rev. Real. Acad. Ciencias exact. Madrid, 1916, **14**, 681; abst. J. S. C. I. 1917, **36**, 299; Bull. Agric. Intell. 1917, **7**, 1256) has reported upon the use of manganese as a catalyst in atmospheric nitrogen fixation by plants through bacterial agency.

2. Badische Anilin u. Soda Fabrik, E. P. 6045, 1900; 12720, 1908; 19249, 1910; abst. C. A. 1912, **6**, 1346; J. S. C. I. 1909, **28**, 788; 1911, **30**, 1116; Chem. Ztg. Rep. 1911, **35**, 575. E. P. 17411, 1911; 1161, 1912; abst. C. A. 1913, **7**, 403, 2288; J. S. C. I. 1912, **31**, 282; 1913, **32**, 289; Chem. Ztg. Rep. 1913, **37**, 247.

3. R. McKee, U. S. P. 1236853, 1917; abst. J. S. C. I. 1917, **36**, 1048. P. Sabatier and J. Senderens (Compt. rend. 1902, **135**, 278; abst. J. S. C. I. 1902, **31**, 1157) have described the direct reduction of nitrogen oxides in contact with reduced nickel. For the action of strontium carbide on nitrogen, see S. Tucker and Y. Wang, Trans. Amer. Electrochem. Soc. 1912, **22**, 67; abst. J. S. C. I. 1913, **32**, 532.

4. Chem. Fabr. Griesheim Elektron, E. P. 14448, 1914; abst. J. S. C. I. 1915, **34**, 962.

5. A. Frank and N. Caro, D. R. P. 224329; abst. Zts. ang. Chem. 1906, **19**, 1569; 1910, **23**, 2098; Chem. Zentr. 1910, **81**, II, 511; Chem. Ztg. Rep. 1910, **34**, 397; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 485; Zts. Schiess. Spreng. 1910, **5**, 338. For the decomposition of feldspar and its use in the fixation of atmospheric nitrogen, see W. Ross, J. Ind. Eng. Chem. 1913, **5**, 725; abst. J. S. C. I. 1913, **32**, 942. See also H. Petersen, Metall. u. Erz. 1916, 197, 204; Chem. Ztg. Rep. 1917, **41**, 70; abst. J. S. C. I. 1917, **36**, 641. •D. Meneghini, Gazz. Chem. Ital. 1913, **43**, 81; J. S. C. I. 1913, **32**, 230.

6. F. Bedford and E. Erdmann, U. S. P. 1200696; abst. J. S. C. I. 1916, **35**, 1156. Kunheim & Co. (D. R. P. 205774, 276986; abst. J. S. C. I. 1909, **28**, 243; 1914, **33**, 1154; Mon. Sci. 1912, **77**, 51; Chem. Zentr. 1909, **80**, I, 803; 1914, **85**, II, 596; Chem. Ztg. Rep. 1914, **38**, 466; Jahr. Chem. 1909, **62**, 370; Wag. Jahr. 1909, **55**, I, 399; 1914, **60**, I, 308; Zts. ang. Chem. 1909, **22**, 358; 1914, **27**, 564) have patented cerium nitride as a catalyst.

7. F. P. 440217, 440218, 1911; abst. C. A. 1912, **6**, 3501; J. S. C. I. 1912, **31**, 722; Chem. Ztg. Rep. 1912, **36**, 514. H. Koppers, D. R. P. 257188, 285354, 1913; abst. J. S. C. I. 1915, **34**, 1142.

8. A. Sinding-Larsen and O. Storm, Swed. P. 36205; Chem. Ztg. Rep. 1914, **38**, 499. Swiss P. 58918, 1911. L. Duparc and C. Urfer, E. P. 133041, 1919; abst. C. A. 1920, **14**, 325.

9. Soc. Generale des Nitrures, E. P. 27030, 27971, 28071, 1913; abst. J. S. C. I. 1914, **33**, 483, 549, 961; C. A. 1914, **8**, 3356; Chem. Ztg. Rep. 1914, **38**, 399. U. S. P. 1198965, 1916; abst. J. S. C. I. 1916, **35**, 1109.

10. R. Tofani, Chem. Trade J. 1913, **53**, 232. A. Wilhelm, D. R. P. 270062; abst. C. A. 1914, **8**, 1892; Chem. Zentr. 1914, **85**, I, 712; Chem. Ztg. Rep. 1914, **38**, 101; Zts. ang. Chem. 1914, **27**, 189.

11. F. Bayer & Co., D. R. P. 168272, 263287, 285698, 286719; J. S. C.

as lead chromate and bone ash¹ have found use under special conditions. E. Andersen² uses Hannover's porous metals³ as the catalytic agent, while the Bremen-Besigheimer Oelfabriken⁴ produce a catalyst of metals, metallic oxides and carbon, by calcining organic metal compounds with carbon to the point where a pyrophoric mixture results.

The Badische Co. have patented, among others, the use of uranium,⁵ osmium,⁶ molybdenum⁷ and titanium.⁸

Nitrides, Cyanides and Cyanamides as Sources of Nitric Acid.—Many processes have been described for the formation of ammonia by the action of steam upon metallic nitrides as those of aluminium,⁹ silicon and titanium,¹⁰ the ammonia being then oxidized into nitric acid as by the methods already described, but as yet these processes have not been developed to a firm commercial basis. The Serpek process is typical of this class of reactions.

While the cyanide processes may, as yet, not be said to be economic successes, yet they offer vast possibilities, due primarily to the simplicity of the chemical reactions involved, and to the fact that but little power is required. It appears at present that

1. 1911, **34**, 1143, 1249; Mon. Sci. 1917, **84**, 78; Chem. Zentr. 1906, **77**, I, 1198; 1913, **84**, II, 827; 1915, **86**, II, 292, 565; Chem. Ztg. Rep. 1906, **30**, 425; 1913, **37**, 515; 1915, **39**, 298, 367; Chem. Zts. 1906, **5**, 344; Jahr. Chem. 1905-1908, I, 1777; Wag. Jahr. 1906, **52**, I, 449; 1913, **59**, I, 515; Zts. ang. Chem. 1906, **19**, 1941; 1913, **26**, 562; 1915, **28**, 424, 471; Zts. Schiess. Spreng. 1906, **1**, 103. D. R. P. 299613, 1917; abst. J. S. C. I. 1920, **39**, 64-A. See also Belg. P. 262321, 1913.

1. C. Parsons, U. S. P. 1239125, 1917; abst. J. S. C. I. 1917, **36**, 1127. C. Parsons and L. Jones, E. P. 136342, 1919; abst. J. S. C. I. 1920, **39**, 108-A.

2. E. P. 7839, 1913; abst. C. A. 1914, **8**, 3223; J. S. C. I. 1914, **33**, 470.

3. E. P. 25702, 1911; abst. C. A. 1913, **7**, 1475; J. S. C. I. 1912, **31**, 648.

4. E. P. 4023, 1914. Compare also Alby United Carbide Factories, E. P. 18207, 1911; F. P. 433306; abst. J. S. C. I. 1911, **30**, 1252; Mon. Sci. 1913, **79**, 130; C. A. 1913, **7**, 404. Aluminium Industrie Akt., F. P. 465807, abst. J. S. C. I. 1914, **33**, 643; 1916, **35**, 1156; C. A. 1914, **8**, 3399; Mon. Sci. 1916, **83**, 13. H. Andriessen and J. Scheidemandel, E. P. 162067, 1912; abst. J. S. C. I. 1912, **31**, 1083; C. A. 1914, **8**, 23. Refer to D. R. P. 283824, 284815, 287009; abst. Chem. Zentr. 1915, **86**, I, 1031; II, 213; 1916, **87**, I, 730; Chem. Ztg. Rep. 1915, **39**, 186, 244, 376; Zts. ang. Chem. 1915, **28**, 295, 363, 521. E. P. 13689, 1914; 13292, 1915; abst. J. S. C. I. 1916, **35**, 1101. Norw. P. 26690, 26691. Swiss P. 72690.

5. Belg. P. 226091, 1910.

6. Belg. P. 222222, 1910.

7. Aust. P. 62524, 1913, addn. to Aust. P. 54243.

8. Swiss P. 44222, 1908; Belg. P. 206905, 1908.

9. O. Serpek, Belg. P. 225952, 1910; Swiss P. 44367, 1908; 57981, 1911.

10. A. Sinding-Larsen, U. S. P. 1042723; E. P. 12314, 1915; F. P. 375342, 414837; abst. J. S. C. I. 1907, **26**, 924; 1910, **29**, 1205; 1911, **32**, 1382; Mon. Sci. 1908, **69**, 85; 1913, **79**, 97; C. A. 1912, **6**, 3169; 1913, **7**, 220. Swiss P. 47929, 48700, 1909.

if certain mechanical difficulties can be surmounted satisfactorily, nitrogen may be fixed in this form more cheaply than in any other process so far brought forward.

In the production of nitric acid and nitrates by means of the cyanamides, cheap power is a requisite for its successful operation. The centers of cyanamide manufacture therefore, have been in the vicinity of large waterfalls, in the Western Hemisphere only at Niagara Falls. It requires, for instance, but about 20% the horse power per ton per year of nitrogen fixed, as is necessary when operating by the arc process.

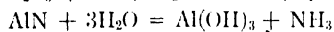
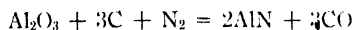
Nitric Acid from Nitriles.¹ The principal process for the formation of nitric acid in this manner is that of O. Serpek,²

1. "Manufacture of nitrogenized compounds of aluminum for the production of nitric acid," U. S. P. 888044, F. P. 367124; abst. J. S. C. I. 1906, **25**, 1096. "Process for making aluminium nitride," U. S. P. 987408, 1016526. E. P. 7507, 1909. F. P. 411031; abst. J. S. C. I. 1910, **29**, 277. "Process for producing ammonia from aluminium nitride," E. P. 15997, 1909. F. P. 415252; abst. J. S. C. I. 1909, **29**, 1126. "Process for making Al-N compounds," E. P. 15995, 1909. F. P. 367124; abst. J. S. C. I. 1910, **29**, 25. "Process of making aluminium nitride," E. P. 15996, 1909. F. P. 415216; abst. J. S. C. I. 1909, **28**, 1198. "Process for the manufacture of aluminium and other metallic nitriles," U. S. P. 996032. E. P. 13086, 1910. F. P. 427109; abst. J. S. C. I. 1911, **30**, 421. "Manufacture of nitriles such as that of aluminium," U. S. P. 1030929, 1044927. E. P. 12601, 1910. F. P. 427066; abst. J. S. C. I. 1911, **30**, 361. "Apparatus for the manufacture of aluminium nitride," E. P. 16522, 1910; F. P. 427066; abst. J. S. C. I. 1911, **30**, 361. "Revolving electrical furnace with resistances arranged diametrically," E. P. 29299, 1910. F. P. 430553; abst. J. S. C. I. 1911, **30**, 905. "Rotary electric furnace, principally for making aluminium nitride," E. P. 29715, 1910. F. P. 430553; abst. J. S. C. I. 1911, **30**, 1222. "Manufacture of nitriles," F. P. 426868; abst. J. S. C. I. 1911, **30**, 1058. "Electric resistance furnace for making aluminium nitride," F. P. 427066; abst. J. S. C. I. 1912, **31**, 32. "Process for the manufacture of aluminium nitride," F. P. 430822; abst. J. S. C. I. 1911, **30**, 1382. "Process for the manufacture of aluminium nitride," U. S. P. 1094171. E. P. 8348, 1912; abst. J. S. C. I. 1913, **32**, 875. "Process for the manufacture of ammonia by means of aluminium nitride," U. S. P. 1040439. E. P. 10036, 1912. F. P. 454430; abst. J. S. C. I. 1912, **31**, 1078. D. R. P. 181991, 181992; abst. Zts. ang. Chem. 1907, **20**, 1376. Zts. ang. Chem. 1914, **27**, I, 41. For the preparation of aluminium nitride, see E. P. 120035, 1918; abst. C. A. 1919, **13**, 367. Soc. Generale des Nitrures, F. P. 435308, 1910; 438209, 1911. E. P. 25141, 1911; 101091, 1916. U. S. P. 1143482, 1915; abst. J. S. C. I. 1912, **31**, 127, 385, 588, 687; 1915, **34**, 423, 824; 1917, **36**, 503. Aust. P. 58193, 1913; Belg. P. 248086, 1912; 256395, 262309, 262419, 1913; Swiss P. 60119, 1911; 60037, 58666, 59148, 65350, 66124, 66640, 67106, 67107, 70283, 70901, 71281, 71590; 71804, 74225. O. Serpek, U. S. P. 1060640, 1217842; E. P. 25141, 1911; F. P. 433995, 1910; abst. J. S. C. I. 1912, **31**, 230; 1913, **32**, 693; 1917, **36**, 503. P. Hershman, U. S. P. 1261526, 1918; abst. C. A. 1918, **37**, 1588. F. Polzeniusz, E. P. 323032, 1902; abst. J. S. C. I. 1903, **22**, 420. L. Gautrelet, F. P. 474503, 1913; abst. J. S. C. I. 1915, **34**, 1091. C. Ellis, E. P. 25630, 1912; abst. J. S. C. I. 1913, **32**, 790.
2. "Nitrogenized Compounds of Aluminum for the Production of

whose patents have been acquired by the Societe Generale des Nitrures,¹ and are being exploited at the present time in France,

- Nitric Acid," U. S. P. 888044, F. P. 367124; abst. J. S. C. I. 1906, **25**, 1096.
 "Aluminum Nitride," U. S. P. 987408, 1016526, E. P. 7507, 1909; F. P. 411031; abst. J. S. C. I. 1910, **29**, 277. "Ammonia from Aluminium Nitride," E. P. 15997, 1909; F. P. 415252; abst. J. S. C. I. 1909, **28**, 1126. E. P. 15995, 1909; F. P. 367124; abst. J. S. C. I. 1910, **29**, 25. Austral. P. 12539, 12559, 1914; 17684, 18489, 18490, 18750, 1910. India P. 340, 1910. "Aluminium Nitride," E. P. 15996, 1909; F. P. 415216; abst. J. S. C. I. 1909, **28**, 1198. U. S. P. 996032, E. P. 13086, 1910; F. P. 427109; abst. J. S. C. I. 1911, **30**, 421. U. S. P. 1030929, 1044927, E. P. 12601, 1910; F. P. 427066; abst. J. S. C. I. 1911, **30**, 361. E. P. 16522, 1910; F. P. 427066; abst. J. S. C. I. 1911, **30**, 361. E. P. 20299, 1910; F. P. 430553; abst. J. S. C. I. 1911, **30**, 905. E. P. 29715, 1910; F. P. 430553; abst. J. S. C. I. 1911, **30**, 1222. F. P. 126868; abst. J. S. C. I. 1911, **30**, 1058. E. P. 127066; abst. J. S. C. I. 1912, **31**, 32. "Manufacture of Aluminium Nitride," F. P. 430822; abst. J. S. C. I. 1911, **30**, 1382. U. S. P. 1094171; E. P. 8348, 1912; abst. J. S. C. I. 1913, **32**, 875. U. S. P. 1040439, E. P. 10036, 1912; F. P. 454430; abst. J. S. C. I. 1912, **31**, 1078; 1913, **32**, 195. D. R. P. 481991; abst. Zts. ang. Chem. 1907, **20**, 1376; 1914, **27**, I, 41. A. Lindbald, E. P. 119243; abst. C. A. 1919, **13**, 96. For nitrogen compounds of tungsten, see Badische Anilin u. Soda Fabrik, D. R. P. 216554, 259617; E. P. 12662, 1911; abst. J. S. C. I. 1912, **31**, 431; 1913, **32**, 657. For process for making stable boron nitride, consult G. Weintraub, U. S. P. 1157271, 1915; E. P. 12377, 1913; abst. J. S. C. I. 1914, **33**, 255; 1915, **34**, 1145.
 1. "Manufacture of Nitrides and Ammonia from Nitrogen," E. P. 5795, 1911; 8349, 1912; F. P. 438218, 450140; abst. J. S. C. I. 1912, **31**, 611. E. P. 3344, 1912; F. P. 437168; abst. J. S. C. I. 1912, **31**, 432. "Process of Making Aluminium Nitride," E. P. 8347, 1912; F. P. 450178; abst. J. S. C. I. 1912, **31**, 816; 1913, **32**, 603; U. S. P. 1060509, 1078313; E. P. 8349, 1912; F. P. 449150; abst. J. S. C. I. 1912, **31**, 875. E. P. 12837, 1912; F. P. 458031; abst. J. S. C. I. 1913, **32**, 1019. E. P. 16406, 1912; F. P. 430553; abst. J. S. C. I. 1912, **31**, 1136. E. P. 22435, 1912; F. P. 427109; abst. J. S. C. I. 1913, **32**, 233. U. S. P. 1155840; F. P. 474330; abst. J. S. C. I. 1915, **34**, 1091. "Process of Fixing Nitrogen by Means of Ferro Aluminium," U. S. P. 1198965; E. P. 27030, 27971, 1913; F. P. 470099, 474322; abst. J. S. C. I. 1915, **34**, 1054; E. P. 10975, 1913; F. P. 457650; abst. J. S. C. I. 1913, **32**, 1010. E. P. 11091, 21366, 1913; F. P. 457723; abst. J. S. C. I. 1913, **32**, 1010. E. P. 22568, 1913; F. P. 474365; abst. J. S. C. I. 1915, **34**, 353. E. P. 23740, 1913; abst. J. S. C. I. 1914, **33**, 613. "Manufacture of Aluminium Nitride," E. P. 24533, 1913; F. P. 474820; abst. J. S. C. I. 1915, **34**, 423. E. P. 24347, 1913; F. P. 463390; abst. J. S. C. I. 1914, **33**, 427. E. P. 28071, 1913; abst. J. S. C. I. 1914, **33**, 483. "Process of Oxidizing Ammonia," E. P. 473618; abst. J. S. C. I. 1915, **34**, 715. E. P. 4287, 1915; F. P. 476121; abst. J. S. C. I. 1915, **34**, 961. E. P. 11271, 1915; F. P. 478886; abst. J. S. C. I. 1916, **35**, 115. F. P. 474322; abst. J. S. C. I. 1916, **35**, 633. "Process of Fixing Atmospheric Nitrogen," F. P. 474365; abst. J. S. C. I. 1916, **35**, 633. F. P. 475908; abst. J. S. C. I. 1916, **35**, 46. F. P. 476121. D. R. P. 238310; abst. J. S. C. I. 1911, **30**, 1313. "Production of Boron Nitride," British Thomson-Houston Co., E. P. 21865, 1912; abst. J. S. C. I. 1913, **32**, 600. In this connection see F. Gros and Bouchardy, E. P. 132622; abst. C. A. 1920, **14**, 254. S. Giertsen, U. S. P. 1326045, 1919; abst. J. S. C. I. 1920, **39**, 174-A. H. Eastman, U. S. P. 1282395, 1917; abst. Chim. Ind. 1920, **3**, 213. G. Cox, U. S. P. 1326422, 1919; abst. C. A. 1920, **14**, 502. E. Metzger, U. S. P. 1322195, 1324119, 1919; abst. C. A. 1920, **14**, 318; J. S. C. I. 1920, **39**, 109-A. Barzano and Zanardo, Ital. P. 381/81/124876; abst. Chem. Ztg. 1913, **37**, 228. C. Burke,

a metallic nitride—preferably aluminium—being formed from alumina, and this subsequently decomposed by water or alkali, according to the following reactions:



Aluminium carbide was first employed as raw material, being heated in a current of nitrogen or generator gas. The addition of carbon or aluminium to the carbide is alleged to increase the absorption of nitrogen. According to the observations of N. Caro, the nitrogen absorption by aluminium carbide is preceded by dissociation of the carbide into aluminium and carbon, the absorption being accelerated by the addition of 5% copper or iron. It has been shown that the yield of nitride is greatly influenced by the temperature employed, and that, while some nitrogen is absorbed at 1100°, more rapidly at 1500°, energetically at 1700°, and with violence at 1800°–1850°, nearly pure nitride was formed only at the more elevated temperatures. However,

H. Boyd, P. Biddison and J. Zink, U. S. P. 1319843, 1919; abst. J. S. C. I. 1919, **38**, 946-A; C. A. 1920, **14**, 101. O. Carlson, Swiss P. 58422; abst. Chem. Ztg. 1913, **37**, 254. G. Contagne, E. P. 12057, 1911; abst. J. S. C. I. 1915, **34**, 80. E. Haslup, E. P. 135885, 135889, 1920. H. Immendorff and H. Kappen, Swiss P. 58408; D. R. P. 257769, 257827; abst. Chem. Ztg. 1913, **37**, 228, 262. H. Kipper, U. S. P. 1322026, 1919; abst. C. A. 1920, **14**, 322. T. Knösch, Aust. P. 58168; abst. Chem. Ztg. 1913, **37**, 262. A. Lindblad, U. S. P. 1328575, 1920; E. P. 122523; abst. C. A. 1920, **14**, 697; Chim. Ind. 1920, **3**, 212. O. Lemmermann and A. Eimecke, Mitt. Dent. Landw.-Ges. 1918, **33**, 574; Bied. Zentr. 1919, **48**, 290; J. S. C. I. 1920, **14**, 75. A. E. Lewis, U. S. P. 1321459, 1911; abst. C. A. 1920, **14**, 211. J. Lidholm, Austral. P. 12783, 12784, 1914; New Zeal. P. 34729, 34730, 1914. V. Maly, Zts. Landw. Versuchsw. Oester. 1916, **19**, 445; Bied. Zentr. 1919, **48**, 369; J. S. C. I. 1920, **39**, 74-A. Meister, Lucius & Brünig, D. R. P. 311018, 311019, 1916; abst. J. S. C. I. 1920, **39**, 174-A. D. Meyer and R. Gorkow, Ill. Landw. Zts. 1919, **39**, 27; abst. Bied. Zentr. 1919, **48**, 370, J. S. C. I. 1920, **39**, 75-A. F. Morani, Ital. P. 380 242 124514; abst. Chem. Ztg. 1913, **37**, 92. Nitrogen Co., Aust. P. 56429, 56430; abst. Chem. Ztg. 1913, **37**, 11. Nitrogen Corporation, E. P. 24307, 1899; 11912, 1900; 27713, 1912; 13332, 1914; 133095, 1918; abst. C. A. 1920, **14**, 1920, **14**, 322. A. Holter, F. P. 460963, 1914; U. S. P. 1203740, 1916; abst. J. S. C. I. 1914, **33**, 865; 1916, **35**, 1261. J. Reid, E. P. 133098, 133099, 133100, 1918; abst. C. A. 1920, **14**, 253. P. Saves, E. P. 135847, 1920. M. Shoeld, Can. P. 195602, 1919; abst. C. A. 1920, **14**, 503. Societe, Piemontese per la fabbricazione de Carbuoro di Calcio Prodotti Affini, Ital. P. 381 236 123943; abst. Chem. Ztg. 1913, **37**, 200. Stickstoffwerke, D. R. P. 258342; abst. Chem. Ztg. 1913, **37**, 326. C. Stutz, E. P. 133106, 1918; abst. C. A. 1920, **14**, 238. F. Slocum, E. P. 133101, 133104, 133105, 1918; abst. C. A. 1920, **14**, 253, 318; J. S. C. I. 1919, **38**, 900-A. N. Testrup and Techno-Chemical Laboratories, Ltd., E. P. 131984, 1918; abst. J. S. C. I. 1920, **14**, 322. V. Thrane, U. S. P. 1326310, 1919; D. R. P. 312088, 1916; abst. C. A. 1920, **14**, 503; Chim. Ind. 1920, **3**, 208.

when temperatures of 2000° and above were employed, formation substantially ceased due to the decomposition of the nitride as fast as formed. According to Serpek, the most favorable temperature for maximum yields lies between 1800° and 1900°. He also found that impure alumina as bauxite and some of the purer clays could be converted, and often at lower temperatures than the purer aluminium compounds, presumably due to the catalytic effect of the impurities.

The Serpek process consists essentially of two superposed cylindrical kilns, oppositely rotating and inclined to each other, the powdered and dried bauxite being introduced into the upper one, and calcined in its descent by means of counterflowing hot gases. The calcined bauxite, drops through a funnel into a chamber where the desired amount of carbon is introduced, then enters the lower cylinder, where in its descent it passes through an electrically heated zone where it is submitted to a temperature of 1800°–1900°. Here the nitrogen reacts with the aluminium and carbon with the formation of AlN and CO. The siliceous impurities are mostly volatilized. The formed nitride is collected in an air-tight chamber. The product from bauxite contains about 26% nitrogen, whereas that from pure alumina contains up to 34%. The methods of K. Kaiser,¹ J. Bucher,² G. Giuliani,³

1. E. P. 26803, 1905; 24035, 1911; abst. J. S. C. I. 1906, **25**, 218. Austral. P. 2331, 1905; 19008, 1910; 3486, 1911. F. P. 435397, 1911; abst. J. S. C. I. 1912, **31**, 385. See C. Krauss and P. Stachlin, U. S. P. 1211181, 1917; abst. J. S. C. I. 1917, **36**, 138. For manufacture of coherent masses of boron and titanium nitrides, see E. Podszus, D. R. P. 282748, 286992, 1913; abst. J. S. C. I. 1915, **34**, 717; 1916, **35**, 176; Chem. Zentr. 1915, **86**, I, 715; 1917, **88**, I, 730; Chem. Ztg. Rep. 1915, **39**, 108, 376; Zts. ang. Chem. 1915, **28**, 205, 508. For preparation of aluminium and magnesium carbonitrides, (cyanamides), consult S. Peacock, E. P. 11390, 1912; F. P. 458168, 1913; abst. J. S. C. I. 1913, **32**, 699, 1067; Mon. Sci. 1914, **81**, 55; Chem. Ztg. Rep. 1914, **38**, 345; C. A. 1913, **7**, 3644. U. S. P. 1057876, 1147184, 1123585; abst. J. S. C. I. 1913, **32**, 487; 1915, **34**, 423, 961; C. A. 1913, **7**, 1781; Mon. Sci. 1913, **79**, 146; Chem. Ztg. Rep. 1915, **39**, 298; 1917, **41**, 34.
2. E. P. 139, 1913; abst. C. A. 1914, **8**, 2547. U. S. P. 1159989; F. P. 465679; abst. J. S. C. I. 1914, **33**, 644; C. A. 1914, **8**, 3491; Mon. Sci. 1916, **83**, 13; Chem. Ztg. Rep. 1914, **38**, 479. Austral. P. 11238, 1913 (C. Hatton and J. Bucher); 13690, 14805, 1914; 15965, 1915. G. Patronilleau, F. P. 475195, 1914; abst. J. S. C. I. 1916, **35**, 46; Mon. Sci. 1916, **83**, 84. For the preparation of silicon nitride, see Badische Co., Belg. P. 222111, 1910; Swiss P. 48342, 1909.
3. U. S. P. 1180840; abst. J. S. C. I. 1916, **35**, 633. D. R. P. 295573, 1912; abst. Chim. Ind. 1920, **3**, 214. F. P. 451405; abst. Chem. Ztg. 1913, **37**, 336. E. P. 25874, 1912; abst. C. A. 1914, **8**, 1491; J. S. C. I. 1913, **32**, 911. F. P. 451405; abst. J. S. C. I. 1913, **32**, 600; C. A. 1913, **7**, 3204; Mon. Sci. 1914, **81**, 7; Chem. Ztg. Rep. 1913, **37**, 378. F. P. 22837, 1913; abst.

J. Margoles,¹ E. Milde,² W. Zaenker,³ and R. Wallace and E. Wasmer,⁴ are similar up to this point.

Irrespective of how obtained, the aluminium nitride can be decomposed by water or dilute alkali, or with sodium aluminate solution according to the Bayer process; or with steam at five atmospheres,⁵ the nitrogen being recovered as ammonia. Where sodium aluminate is used, a highly purified alumina, free from iron and silica is obtained, of especial value in the electrolytic production of aluminium.

G. Coutagne,⁶ P. Hershman,⁷ T. Hygen,⁸ and A. Sinding-Larsen,⁹ have evolved refinements of this general process. The

J. S. C. I. 1915, **34**, 800; F. P. 463232; abst. J. S. C. I. 1914, **33**, 421; C. A. 1914, **8**, 2464; Mon. Sci. 1916, **83**, 10; Chem. Ztg. Rep. 1914, **38**, 237.

1. F. P. 465365; abst. J. S. C. I. 1914, **33**, 549.

2. U. S. P. 1115003; abst. J. S. C. I. 1914, **33**, 1207; Mon. Sci. 1915, **82**, 18. See Badische Co., Swiss P. 51114, 51115, 51741, 1910.

3. F. P. 459093; abst. J. S. C. I. 1913, **32**, 1155; C. A. 1914, **8**, 2463; Chem. Ztg. Rep. 1914, **38**, 170. F. P. 458519; abst. J. S. C. I. 1913, **32**, 1108; C. A. 1914, **8**, 2463; Chem. Ztg. Rep. 1914, **38**, 177.

4. E. P. 18450, 1912; abst. C. A. 1914, **8**, 556; J. S. C. I. 1914, **33**, 22. For method of producing molded blocks of nitrides, see E. Podazus, Holl. P. 2517, 1918; abst. C. A. 1919, **13**, 503; E. P. Appl. 21378, 1913. Consult P. Hershman, U. S. P. 1261526, 1918; abst. J. S. C. I. 1918, **37**, 415-A.

5. S. Peacock, U. S. P. 1035727; E. P. 11395, 1912; abst. J. S. C. I. 1912, **31**, 875; 1913, **32**, 657; C. A. 1912, **6**, 3315; 1913, **7**, 3644; Mon. Sci. 1913, **79**, 4; Chem. Ztg. Rep. 1912, **36**, 581. U. S. P. 1031581, 1031582; E. P. 11391, 11393, 1912; abst. J. S. C. I. 1912, **31**, 773; 1913, **32**, 657; C. A. 1912, **6**, 2676; 1913, **7**, 3644; Mon. Sci. 1913, **79**, 3, 746; Chem. Ztg. Rep. 1912, **36**, 662. U. S. P. 1092167; abst. J. S. C. I. 1915, **34**, 176; C. A. 1914, **8**, 1857; Mon. Sci. 1914, **81**, 100; Chem. Ztg. Rep. 1914, **38**, 361. U. S. P. 1129512, 1129513; abst. J. S. C. I. 1915, **34**, 365. F. P. 448550; abst. J. S. C. I. 1913, **32**, 363; Mon. Sci. 1914, **81**, 4. Trans. Amer. Electrochem. Soc. 1915, **27**, 409.

6. U. S. P. 1158899, E. P. 12057, 1913; F. P. 469554; abst. J. S. C. I. 1915, **34**, 80; 1916, **35**, 633. F. P. 436710; abst. J. S. C. I. 1912, **31**, 432; C. A. 1912, **6**, 2502; Mon. Sci. 1913, **79**, 134; Chem. Ztg. Rep. 1912, **36**, 330. F. P. 436789; abst. J. S. C. I. 1912, **31**, 432, 544, 922. F. P. 437504; abst. J. S. C. I. 1912, **31**, 535, 1032. F. P. 437789; abst. J. S. C. I. 1912, **31**, 432. F. P. 477746; abst. J. S. C. I. 1916, **35**, 633; Mon. Sci. 1916, **83**, 87. F. P. 466986, 1913; J. S. C. I. 1914, **33**, 865; Mon. Sci. 1916, **83**, 15. M. Shoeld, U. S. P. 1274797, 1918; abst. C. A. 1918, **12**, 1950; J. S. C. I. 1918, **37**, 662-A.

7. U. S. P. 1188651; abst. J. S. C. I. 1916, **35**, 890; Chem. Ztg. Rep. 1917, **41**, 124. U. S. P. 1188769; abst. J. S. C. I. 1916, **35**, 890. U. S. P. 1188770; abst. J. S. C. I. 1916, **35**, 890. U. S. P. 1188771; abst. J. S. C. I. 1916, **35**, 890. Can. P. 175751, 1917; abst. C. A. 1917, **11**, 3103.

8. F. P. 482250; abst. C. A. 1917, **11**, 3394.

9. U. S. P. 1042723, F. P. 418837; abst. J. S. C. I. 1910, **29**, 1205; C. A. 1913, **7**, 220; Mon. Sci. 1913, **79**, 97. U. S. P. 1031477, E. P. 12314, 1911; F. P. 431182; abst. J. S. C. I. 1911, **30**, 1382; Mon. Sci. 1913, **79**, 15, 129; C. A. 1912, **6**, 2580, 3169. F. P. 375342; abst. J. S. C. I. 1907, **26**, 924; Mon. Sci. 1908, **77**, 85.

Badische Anilin u. Soda Fabrik¹ produce nitrates by treating nitrides with nitric acid or with the gases containing nitrogen oxides from an electric arc furnace.

The purely scientific side of the Serpek process has been investigated by S. Tucker and H. Read,² W. Fraenkel,³ J. Rich-

1. E. P. 28614, 1904; 11274, 1909; abst. J. S. C. I. 1905, **24**, 619; 1910, **29**, 757. L. Roth, Swiss P. 38927, 1906.
2. Trans. Amer. Electrochem. Soc. 1912, **22**, 57; abst. C. A. 1913, **7**, 25, 1673. S. Tucker, Coal Trades Review, 1913, **11**, 476; J. S. C. I. 1913, **32**, 1143; Jour. Ind. Eng. Chem. 1913, **5**, 191.
3. Zts. Elektrochem. 1913, **19**, 362. For other methods for producing nitrides, see D. R. P. 66806; abst. Ber. 1893, **26**, 350; Wag. Jahr. 1893, **39**, 425; Zts. ang. Chem. 1893, **6**, 151. D. R. P. 66813; abst. Ber. 1893, **26**, 428; Wag. Jahr. 1913, **39**, 425; Zts. ang. Chem. 1893, **6**, 151. D. R. P. 88999; abst. Mon. Sci. 1913, **79**, 741; Chem. Centr. 1897, **68**, I, 142; Chem. Ztg. Rep. 1896, **20**, 934; Jahr. Chem. 1897, **50**, 529; Wag. Jahr. 1896, **42**, 411; Zts. ang. Chem. 1896, **9**, 670. D. R. P. 117623; abst. Mon. Sci. 1901, **57**, 156; 1915, **82**, 19; Chem. Centr. 1901, **72**, I, 347; Chem. Ztg. Rep. 1901, **25**, 137; Wag. Jahr. 1901, **47**, II, 18; Zts. ang. Chem. 1901, **14**, 200. D. R. P. 197393; abst. Mon. Sci. 1911, **75**, 90; Chem. Zentr. 1908, **79**, I, 1747; Chem. Ztg. Rep. 1908, **32**, 304; Chem. Zts. 1908, **7**, 868; Jahr. Chem. 1905-1908, I, 1721; Wag. Jahr. 1908, **54**, I, 467; Zts. ang. Chem. 1908, **21**, 1371. D. R. P. 203750; abst. Mon. Sci. 1912, **77**, 49; Chem. Zentr. 1908, **79**, II, 1655; Chem. Ztg. Rep. 1908, **32**, 623; Chem. Zts. 1909, **8**, 1031; Jahr. Chem. 1905-1908, I, 2186; Wag. Jahr. 1908, **54**, I, 470; Zts. ang. Chem. 1909, **22**, 271. D. R. P. 205683; abst. Chem. Zentr. 1909, **80**, I, 804; Chem. Ztg. Rep. 1909, **33**, 33; Jahr. Chem. 1909, **62**, 542; Wag. Jahr. 1909, **55**, I, 500; Zts. ang. Chem. 1909, **22**, 362. D. R. P. 216745; abst. Mon. Sci. 1910, **73**, 152; Chem. Zentr. 1910, **81**, I, 212; Chem. Ztg. Rep. 1909, **33**, 666; Jahr. Chem. 1909, **62**, I, 744; Wag. Jahr. 1909, **55**, I, 471; Zts. ang. Chem. 1910, **23**, 228. D. R. P. 217037; abst. Chem. Zentr. 1910, **81**, I, 306; Chem. Ztg. Rep. 1910, **34**, 19; Chem. Zts. 1910, **9**, No. 1669; Jahr. Chem. 1909, **62**, I, 644; Wag. Jahr. 1909, **55**, I, 472; Zts. ang. Chem. 1910, **23**, 378. D. R. P. 224628; abst. Mon. Sci. 1914, **81**, 88; Chem. Zentr. 1910, **81**, II, 697; Chem. Ztg. Rep. 1910, **34**, 115; Chem. Zts. 1911, **10**, No. 2184; Jahr. Chem. 1910, **63**, I, 794; Wag. Jahr. 1910, **56**, I, 517; Zts. ang. Chem. 1910, **23**, 2292. D. R. P. 229638; abst. Mon. Sci. 1914, **81**, 84; Chem. Zentr. 1911, **82**, I, 273; Chem. Ztg. Rep. 1911, **35**, 43; Wag. Jahr. 1911, **57**, I, 508; Zts. ang. Chem. 1911, **24**, 183. D. R. P. 231090; abst. Mon. Sci. 1914, **81**, 148; Chem. Zentr. 1911, **82**, I, 696; Chem. Ztg. Rep. 1911, **35**, 127; Wag. Jahr. 1911, **57**, I, 462; Zts. ang. Chem. 1911, **24**, 522. D. R. P. 231886; abst. Mon. Sci. 1914, **81**, 148; Chem. Zentr. 1911, **82**, I, 852; Chem. Ztg. Rep. 1911, **35**, 129; Wag. Jahr. 1911, **57**, I, 506; Zts. ang. Chem. 1911, **24**, 565. D. R. P. 234129; abst. Chem. Zentr. 1911, **82**, I, 1467; Wag. Jahr. 1911, **57**, I, 507; Zts. ang. Chem. 1911, **24**, 1002; Zts. Schiess. Spreng. 1911, **6**, 315. D. R. P. 235213; abst. C. A. 1912, **6**, 1825; Chem. Zentr. 1911, **82**, II, 111; Chem. Ztg. Rep. 1911, **35**, 353; Wag. Jahr. 1911, **59**, I, 506; Zts. ang. Chem. 1911, **24**, 1442. D. R. P. 235669; abst. Chem. Zentr. 1911, **82**, II, 169; Chem. Ztg. Rep. 1911, **35**, 347; Wag. Jahr. 1911, **57**, I, 507; Zts. ang. Chem. 1911, **24**, 1443. D. R. P. 236044; abst. Chem. Zentr. 1911, **82**, II, 238; Chem. Ztg. Rep. 1911, **35**, 363; Wag. Jahr. 1911, **57**, I, 507; Zts. ang. Chem. 1911, **24**, 1443. D. R. P. 237436; abst. C. A. 1912, **6**, 1507; Chem. Zentr. 1911, **82**, II, 650; Chem. Ztg. Rep. 1911, **35**, 443; Wag. Jahr. 1911, **57**, I, 505; Zts. ang. Chem. 1911, **24**, 1782. D. R. P. 238340; abst. C. A. 1912, **6**, 1575; Chem. Zentr. 1911, **82**, II, 1077; Chem. Ztg. Rep. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 505; Zts.

ards,¹ and described in detail by T. Norton, Donath and Indra, and J. Knox.²

Cyanides and Cyanamides as Sources of Nitric Acid. H. Moisson in 1892 demonstrated that calcium carbide could be readily produced in large quantities in the electric furnace, and in 1895 A. Frank and N. Caro³ published their investigations on nitrogen absorption by metallic carbides, which laid the foundation for the cyanamide industry on its present solid technical basis. According to Moisson, calcium carbide does not absorb

ang. Chem. 1911, **24**, 2029; D. R. P. 239909; abst. C. A. 1912, **6**, 2149; Chem. Zentr. 1911, **82**, II, 1620; Chem. Ztg. Rep. 1911, **35**, 626; Wag. Jahr. 1911, **57**, I, 503; Zts. ang. Chem. 1911, **24**, 2276; D. R. P. 243839; abst. C. A. 1912, **6**, 2299; Chem. Zentr. 1912, **83**, I, 865; Chem. Ztg. Rep. 1916, **36**, 171; Wag. Jahr. 1912, **58**, I, 457; Zts. ang. Chem. 1912, **25**, 595; D. R. P. 246554; abst. C. A. 1912, **6**, 2504; Chem. Zentr. 1912, **83**, I, 1645; Chem. Ztg. Rep. 1912, **36**, 291; Wag. Jahr. 1912, **58**, I, 458; Zts. ang. Chem. 1912, **25**, 1651; D. R. P. 250377; abst. C. A. 1912, **6**, 3502; Chem. Zentr. 1912, **83**, II, 1168; Chem. Ztg. Rep. 1912, **36**, 523; Wag. Jahr. 1912, **58**, I, 458; Zts. ang. Chem. 1912, **25**, 2380.

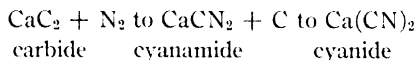
1. Chem. Eng. 1913, **17**, 113, 196. Trans. Amer. Electrochem. Soc. 1913, **33**, 351.

2. Compare C. Thorssell and H. Lunden, U. S. P. 1286839, 1918; abst. C. A. 1919, **13**, 366.

3. U. S. P. 996011, 987674, 1010404; E. P. 21786, 1907; abst. J. S. C. I. 1908, **27**, 898; C. A. 1912, **6**, 414; Mon. Sci. 1911, **75**, 113; 1912, **77**, 130; Chem. Ztg. Rep. 1911, **35**, 248, 392; U. S. P. 1006927; E. P. 5314, 1907; abst. J. S. C. I. 1908, **27**, 749; C. A. 1912, **6**, 135; Mon. Sci. 1912, **77**, 129; Chem. Ztg. Rep. 1911, **35**, 626; D. R. P. 224329; abst. J. S. C. I. 1910, **29**, 1010; Chem. Zentr. 1910, **81**, II, 711; Chem. Ztg. Rep. 1910, **34**, 397; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 485; Zts. ang. Chem. 1910, **23**, 2008; Zts. Schiess. Spreng. 1910, **5**, 338; D. R. P. 134289, 1900; abst. Zts. ang. Chem. 1902, **15**, 935; Mon. Sci. 1903, **59**, 73; Chem. Zentr. 1902, **73**, II, 774; Chem. Zts. 1903, **2**, 219, 305; Jahr. Chem. 1902, **55**, 373; Wag. Jahr. 1902, **48**, I, 325; Zts. ang. Chem. 1902, **15**, 935; D. R. P. 204882; Aust. P. 49226, 1911; Mon. Sci. 1912, **77**, 50; Chem. Zentr. 1909, **80**, I, 323; Chem. Ztg. Rep. 1909, **33**, 12; Chem. Zts. 1909, **8**, No. 1087; Jahr. Chem. 1909, **62**, 511; Wag. Jahr. 1908, **54**, I, 492; Zts. ang. Chem. 1909, **22**, 457; A. Frank, Zts. ang. Chem. 1903, **16**, 536; 1905, **18**, 1734; 1906, **19**, 835; J. S. C. I. 1908, **27**, 1093; N. Caro, Zts. ang. Chem. 1909, **22**, 1178; A. Frank, Trans. Faraday Soc. 1908, **4**, 99; abst. J. S. C. I. 1908, **27**, 1093; G. Erlwein, Zts. ang. Chem. 1903, **16**, 533; Zts. Elektrochem. 1903, **12**, 551; A. Frank and N. Caro, D. R. P. 108971, 1898; abst. Zts. ang. Chem. 1900, **13**, 145; Chem. Ztg. 1900, **24**, 177; Chem. Zts. 1902, **1**, 219; 1903, **2**, 219; Jahr. Chem. 1900, **53**, 307; 1901, **54**, 321; 1904, **57**, 558; Wag. Jahr. 1900, **46**, II, 30; Zts. ang. Chem. 1900, **13**, 145; D. R. P. 224329; O. Frank and A. Finke, U. S. P. 1101424; abst. C. A. 1914, **8**, 2925; Chem. Ztg. Rep. 1915, **39**, 244; F. P. 439244; abst. Mon. Sci. 1913, **79**, 177. For details of the Muscle Shoals cyanamide nitrate plant, consult Chem. Met. Eng. 1919, **20**; Elect. Rev. 1918, **74**, 52; abst. C. A. 1919, **13**, 284, 399; F. Foerster and H. Jacoby, Zts. Elektrochem. 1907, **13**, 101; 1909, **15**, 820; J. S. C. I. 1907, **26**, 423; W. Landis, Met. Chem. Eng. 1916, **14**, 87; J. Ind. Eng. Chem. 1916, **8**, 156; E. Landis, Zts. Gahrungsphysiol. 1914, **5**, 16; Bull. Agric. Intell. 1914, **6**, 673; J. S. C. I. 1915, **34**, 844.

nitrogen even at 1200°, but Frank and Caro demonstrated that technical alkaline earth carbides, owing to the impurities contained therein, absorb nitrogen at much lower temperatures.

By the action of nitrogen upon metallic carbides, mixtures of cyanides and cyanamides result, the relative proportion depending upon the metal and on the temperature of union. The formation of cyanamide may be expressed as follows:



It has been shown that with alkali carbides there is a large preponderance of cyanide. With BaC_2 about 30% cyanide and 70% cyanamide is formed at 700°–800°, while with CaC_2 , cyanamide only is usually formed. In general the proportion of cyanide increases as the temperature becomes more elevated. C. Matignon¹ has calculated the equilibria theoretically, while Erlwein, Warth and Bentner,² and Bredig, Fraenkel and Wilke³ have studied the catalytic acceleration of cyanide formation. Polzenius,⁴ O. Carlson⁵ and others⁶ have measured the rate of ab-

1. Chem. Ztg. 1914, **38**, 894, 909; abst. J. S. C. I. 1914, **33**, 829. See E. Pranke, Chem. Eng. 1913, **17**, 113. See S. Cloez and S. Cannizzaro, Compt. rend. 1851, **32**, 62; Ann. 1851, **78**, 229. N. Caro, B. Schüick and R. Jacoby, Zts. ang. Chem. 1910, **23**, 2405, 2417. Y. Morimoto, Jap. J. Chem. Ind. 1918, **21**, 881; abst. C. A. 1919, **13**, 363. Bucher, C. A. 1917, **11**, 1020.
2. Ulpiani, Gaz. chim. ital. 1872, **2**, 358–417.
3. C. Acker, U. S. P. 914100, and Reissue 13316, 1911 thereon; 1018802, 1019002, 1072373, 1160811; F. P. 425699, 1910; abst. J. S. C. I. 1910, **29**, 371; 1911, **30**, 956, 1451; 1912, **31**, 334, 335; 1913, **32**, 944; 1915, **34**, 1250.
4. G. Liberi, Ann. R. Staz. Chim. Agrar. Sper. Roma, 1911, (2), **5**.
5. F. P. 417054; abst. C. A. 1912, **6**, 1884; Chem. Ztg. Rep. 1910, **34**, 632. M. Schoeld, U. S. P. 1287472, 1918; abst. C. A. 1919, **13**, 367.
6. C. Morselli, Chem. Trade J. 1918, **63**, 182; abst. C. A. 1919, **13**, 62. For the simultaneous production of calcium cyanamide and P_2O_5 , see E. Haslup, U. S. P. 1281363, 1918; abst. C. A. 1919, **13**, 95. Compare Aktiebolaget Nitrogenium, Swiss P. 77932, 1918; abst. C. A. 1919, **13**, 96; Swed. P. 43668, 1918; abst. C. A. 1919, **13**, 288. See also E. P. 15934, 1912; F. P. 445826, 1912; abst. J. S. C. I. 1912, **31**, 1179; 1913, **32**, 142. For alteration of "lime nitrogen" on storage, see J. Van Zyl, Zts. ang. Chem. 1918, **31**, 1, 203; abst. C. A. 1919, **13**, 245. G. Cox, U. S. P. 1282381, 1918; abst. C. A. 1919, **13**, 95. H. Freeman, U. S. P. 1282405, 1918; abst. C. A. 1919, **13**, 165. H. Eastman, U. S. P. 1282395; abst. C. A. 1919, **13**, 166. For other similar processes consult: Nitrogen Corporation, E. P. 11797, 1913, Appl. 3415, 1917; abst. J. S. C. I. 1918, **37**, 139 A; U. S. P. 1116559, 1914, J. S. C. I. 1914, **33**, 749, 1207. V. Thrane, U. S. P. 1273600, 1918; D. R. P. 302583, 1916; abst. C. A. 1918, **12**, 1915; J. S. C. I. 1918, **37**, 581-A, 416-A. J. Tcherniac, U. S. P. 781472, 1905; E. P. 17449, 1903, 17976, 1902; F. P. 330308, 1903; abst. J. S. C. I. 1905, **24**, 197; 1904, **23**, 714; 1903, **22**, 1045, 1087. L. Summers, U. S. P. 1013460, 1033842, 1912; abst. J. S. C. I. 1912, **31**, 281, 816. H. Sulzer, E. P. 784, 1912; D. R. P. 243797, 1911; abst. J. S. C. I. 1912, **31**, 817, 385. A. Spencer and K. McElroy, U. S. P. 1156108,

sorption of calcium carbide in the presence of nitrogen.

Technical Production of Cyanamides. In addition to the Frank and Caro method, many modifications have been patented 1915; abst. J. S. C. I. 1915, **34**, 1144. M. Sem, U. S. **10**, 1256935, 1918; abst. J. S. C. I. 1918, **37**, 242-A. E. Rossiter, H. Crowther and G. Albright, E. P. 4403, 6226, 1901; abst. J. S. C. I. 1902, **21**, 173, 345. G. Ottermann, U. S. P. 701604, 1902; abst. J. S. C. I. 1902, **21**, 914. G. Mueller, D. R. P. 196372, 1907; abst. J. S. C. I. 1908, **27**, 448. F. Morris, J. Raine, J. Kerr and C. McLachlan, E. P. 24864, 1907; U. S. P. 871948, 1907; abst. J. S. C. I. 1908, **27**, 685; 1907, **26**, 1279. A. Lindblad, E. P. 119243, 1918; 22852, 1914; 4553, 17342, 1909; F. P. 476615, 1914; abst. C. A. 1919, **13**, 96; J. S. C. I. 1915, **34**, 905; 1909, **28**, 1047, 1145; 1910, **29**, 95; 1915, **34**, 1250. J. Johnson, E. P. 2133, 1907; 12662, 1911; 24012, 24117, 1914; F. P. 375357, 1907; abst. J. S. C. I. 1908, **27**, 225; 1912, **31**, 431; 1916, **35**, 71; 1915, **34**, 924; 1907, **26**, 924. G. Johnson, E. P. 3329, 1901; 820, 1900; abst. J. S. C. I. 1902, **21**, 345; 1901, **20**, 1113. C. Jacobs, U. S. P. 719223, 1903; abst. J. S. C. I. 1903, **22**, 297. J. Grossmann, E. P. 36, 1903; F. P. 331331, 1903; abst. J. S. C. I. 1903, **22**, 1194, 1130. A. Godwin and F. Keil, E. P. 2456, 1902; abst. J. S. C. I. 1902, **21**, 1278. W. Feld, E. P. 321225, 1902; E. P. 26396, 1901; abst. J. S. C. I. 1903, **22**, 212, 145. G. Erlwein and A. Frank, U. S. P. 708333, 1902; abst. J. S. C. I. 1902, **21**, 1232. L. Devaueille and F. Bensa, E. P. 12946, 1915; F. P. 478919, 1914; abst. J. S. C. I. 1918, **37**, 546-A; 1916, **35**, 1109 (Ref. E. P. 433, 1882). J. Baxeres De Alzugaray, E. P. 4448, 1903; abst. J. S. C. I. 1903, **22**, 326. J. Darling, U. S. P. 698462, 698463, 698464, 1902; E. P. 9350, 1900; abst. J. S. C. I. 1902, **21**, 773; 1901, **20**, 717. C. Cross, E. P. 28077, 1902; abst. J. S. C. I. 1903, **22**, 1347; E. P. Appl. 3679, 1903; abst. J. S. C. I. 1903, **22**, 327. A. Clemm, U. S. P. 845851, 848612, 1907; F. P. 363893, 1906; abst. J. S. C. I. 1907, **26**, 469; 1906, **25**, 884. K. Burkheiser, E. P. 15742, 1912; F. P. 445556, 1912; abst. J. S. C. I. 1913, **32**, 700, 23. J. Buch, U. S. P. 1032988, 1912; abst. J. S. C. I. 1912, **31**, 773. C. Beindl, U. S. P. 1144457, 1915; D. R. P. 216264, 1908; abst. J. S. C. I. 1915, **34**, 834; 1909, **28**, 1314. H. Blackmore, U. S. P. 889096, 889097, 1908; abst. J. S. C. I. 1908, **27**, 685. K. Bosch and A. Mittasch, U. S. P. 879030, 1908; 1061725, 1913; F. P. 370420, 1906; E. P. 12662, 1911; abst. J. S. C. I. 1908, **27**, 225; 1913, **32**, 603; 1907, **27**, 255; 1912, **31**, 431. J. Bucher, First Addn., 1914, to F. P. 459853, 1913; U. S. P. 1138190, 1915; 1094976, 1914; 1120682, 1914; E. P. 2286, 1915; F. P. 455799, 1912; abst. J. S. C. I. 1915, **34**, 1055, 661; 1914, **33**, 692; 1915, **34**, 176; 1903, **22**, 422; 1913, **32**, 943. Buckle, E. P. 6449, 1912; abst. J. S. C. I. 1912, **31**, 15. G. Erlwein, D. R. P. 199973, 1906; abst. J. S. C. I. 1908, **27**, 981. Badische Anilin u. Soda Fabrik, D. R. P. 259648, 259649, 1912, addns. to D. R. P. 246554; E. P. 12662, 1911; abst. J. S. C. I. 1913, **32**, 657; 1912, **31**, 431; E. P. 12845, 14114, 1912; J. S. C. I. 1913, **32**, 363; 1914, **33**, 920; India P. Appl. 77, 1908; 272, 273, 1907. H. Sulzer, F. P. 438065, 1912; D. R. P. 243797, 1911; abst. J. S. C. I. 1912, **31**, 588, 385. H. Burgevin, F. P. 440331, 1911; abst. J. S. C. I. 1912, **31**, 875. A.-G.-fur Stickstoffdunger, F. P. 450435, 1912; abst. J. S. C. I. 1913, **32**, 601. N. Lecesne, F. P. 472959, 1913, First addn., Aug. 30, 1913; abst. J. S. C. I. 1915, **34**, 552. Soc. Generale des Nitrures, F. P. 473018, 1913, First addn. Oct. 27, 1913; E. P. 24731, 1913; abst. J. S. C. I. 1915, **34**, 786; 1914, **33**, 421. J. Roussel, F. P. 478832, 1915; abst. J. S. C. I. 1916, **35**, 1229. Lindblad, E. P. 15113, 1917; abst. J. S. C. I. 1918, **37**, 611-A. Soc. Generale des Nitrures, E. P. 10450, 1916; abst. J. S. C. I. 1917, **36**, 29. C. Thorssell, E. P. 11485, 1915; abst. J. S. C. I. 1915, **34**, 1207. C. Acker, U. S. P. 1051303, 1913; abst. J. S. C. I. 1913, **32**, 234. C. Greenstreet, U. S. **14**, 1052815, 1913; abst. J. S. C. I. 1913, **32**, 289. G. Erlwein and K. Warth, U. S. P. 994095, 1911; abst. J. S. C. I. 1911, **30**, 803. Societe des Produits Azotecs, F. B. Addn. 2230, 1918. Cyanid Ges., Belg. P. 164577,

from time to time. The Dettifos Power Co. and J. Lidholm¹ treat CaC_2 and N in a rotary tube furnace, the N, supplied under pressure, being used as a driving agent for circulating the gas in the furnace. W. Dreaper² reacts upon CaC_2 with N or NH_3 , the heating being effected by surface combustion, the products of combustion not being allowed to come in contact with the reaction mixture. T. Fujiyama³ in manufacturing nitrogen compounds from carbides without the application of external heat, causes the union by the ignition of a quantity of carbide in an unheated chamber in the presence of air, introducing N when the temperature has risen sufficiently. The essence of the invention of W. Heys⁴ is the use of a reactive metal which has a greater affinity for C and N than has the alkali metal, barium, lithium, calcium, strontium, manganese and aluminium being specified. In another method⁵ cyanamides are produced from carbide by adding halogen salts to molten carbide as it flows from the furnace, or by adding the salts directly to the furnace in which the carbide is produced. The methods of B. de Zanardo,⁶ F. Wash-

1. E. P. 28524, 1913; abst. C. A. 1914, **8**, 2444; J. S. C. I. 1914, **33**, 256; 1915, **34**, 230; Mon. Sci. 1917, **84**, 35; Chem. Ztg. 1914, **38**, 230; Zts. ang. Chem. 1915, **28**, I, 208. E. P. 28629, 1913; abst. J. S. C. I. 1915, **34**, 230. E. P. 3545, 1914; abst. C. A. 1915, **9**, 2037; J. S. C. I. 1915, **34**, 661. E. P. 3546, 1914; abst. C. A. 1915, **9**, 2037. E. P. 3547, 1914; abst. C. A. 1915, **9**, 2037; J. S. C. I. 1914, **33**, 962. Swed. P. 42411, 1917; abst. C. A. 1917, **11**, 2643. E. P. 465379, 468128, 465473, 469045, 469046, 1914; abst. J. S. C. I. 1914, **33**, 962; Mon. Sci. 1916, **83**, 63. U. S. P. 1125350, 1915; abst. J. S. C. I. 1915, **34**, 230. Refer to E. P. 2514, 1874; 15306, 1899; 9522, 1905; 19870, 1906. For "cyanamide hydrolysis," see E. P. 120034, 1918; abst. C. A. 1919, **13**, 365.

2. E. P. 12927, 1913; abst. C. A. 1914, **8**, 3842; J. S. C. I. 1914, **33**, 788. A. Osterberg and E. Kendall, J. Biol. Chem. 1917, **32**, 297; J. S. C. I. 1918, **37**, 107-A.

3. E. P. 9259, 1914; U. S. P. 1126000, 1915; abst. J. S. C. I. 1915, **34**, 283; Chem. Ztg. Rep. 1916, **40**, 15. F. P. 471377, 1914; abst. J. S. C. I. 1915, **34**, 356.

4. E. P. 21628, 1910; abst. J. S. C. I. 1912, **31**, 28; Chem. Ztg. Rep. 1912, **36**, 91. Aktiebolaget Nitrogenium, Swiss P. 77932; abst. C. A. 1919, **13**, 96. T. Allen, U. S. P. 1093819, 1914; abst. J. S. C. I. 1914, **33**, 593; C. A. 1914, **8**, 2039; Mon. Sci. 1914, **81**, 137.

5. K. Schick, U. S. P. 1008927; abst. J. S. C. I. 1911, **30**, 1313; C. A. 1912, **6**, 196. F. P. 430060; Mon. Sci. 1913, **79**, 127. K. Schick and Akt. Ges. für Stickstoffdünger, E. P. 12555, 1911; abst. C. A. 1912, **6**, 3062; J. S. C. I. 1912, **31**, 72.

6. U. S. P. 1164087; abst. J. S. C., I. 1916, **35**, 116. F. P. 456826;

burn,¹ R. Wallace and E. Wasmer,² C. White,³ G. Scialoja,⁴ J. Stillesen,⁵ J. de Ruitjes,⁶ C. McCourt and C. Ellis,⁷ and H. Meyer and J. Stillesen⁸ are similar.⁹

To concentrate cyanamide,¹⁰ the calcium from a solution of calcium cyanamide may be precipitated, the resulting solution of free cyanamide being used as a solvent for dissolving a further quantity of the calcium salt. To prepare CaCN_2 in a granular form¹¹ and

abst. J. S. C. I. 1913, **32**, 1108; C. A. 1914, **8**, 1921; Chem. Ztg. Rep. 1914, **38**, 103.

1. U. S. P. 999071, 1004509; abst. C. A. 1912, **6**, 194; J. Soc. Dyers Col. 1911, **27**, 266; Mon. Sci. 1912, **77**, 155; Chem. Ztg. Rep. 1911, **35**, 545, 575. Eng. News, 1915, **73**, 16; abst. Met. Chem. Eng. 1915, **13**, 309. Trans. Amer. Electrochem. Soc. 1915, **27**, 385.

2. E. P. 14631, 1911; abst. C. A. 1913, **7**, 222; J. S. C. I. 1912, **31**, 1031.

3. E. P. 17937, 1913; abst. J. S. C. I. 1915, **34**, 28.

4. E. P. 22231, 1911; abst. C. A. 1913, **7**, 941; J. S. C. I. 1912, **31**, 775. F. P. 434953, 1911; abst. J. S. C. I. 1912, **31**, 334. Swiss P. 57540; abst. Chem. Ztg. 1913, **37**, 44.

5. U. S. P. 982311; abst. Mon. Sci. 1911, **75**, 122; Chem. Ztg. Rep. 1911, **35**, 180.

6. Onders. Rykslandbouproefstat, 1913, No. 13; abst. J. C. S. 1913, **108**, i, 764; J. S. C. I. 1915, **34**, 972.

7. E. P. 25629, 1912; abst. C. A. 1914, **8**, 1498; J. S. C. I. 1913, **32**, 751; Chem. Ztg. Rep. 1914, **38**, 171.

8. U. S. P. 982288; abst. Mon. Sci. 1911, **75**, 122.

9. For other process for manufacture of cyanamides see: E. P. 25475, 1898; abst. Mon. Sci. 1900, **56**, 186. E. P. 21819, 21820, 1900; abst. J. S. C. I. 1901, **20**, 1113, 1139. E. P. 3328, 3329, 1900; 1841, 1908; abst. J. S. C. I. 1908, **27**, 1152. E. P. 228, 21623, 1910; abst. J. S. C. I. 1911, **30**, 489; 1912, **31**, 28; Chem. Ztg. Rep. 1912, **36**, 91.

10. H. Immendorff and H. Kappen, E. P. 17018, 1911; abst. C. A. 1913, **7**, 399; J. S. C. I. 1912, **31**, 358. For the E. Merck process for preparing cyanaminoformic esters by the interaction of halogenated aminoformic esters with cyanamide, see D. R. P. 247453, 1911; abst. J. S. C. I. 1912, **31**, 796.

11. F. MacMahon, E. P. 9412, 1912; abst. C. A. 1913, **7**, 3383; J. S. C. I. 1912, **31**, 548.

In an apparatus for granulating calcium cyanamide (E. P. 15713, 1913; abst. J. S. C. I. 1914, **33**, 933) a paste of finely ground calcium cyanamide and water is fed through a hopper containing a stirring device on to the surface of a rotating fluid cylinder, which is heated by means of steam to about 95°. A scraper is fitted with teeth, engaging with the grooves of the cylinders, removes the material in the form in which it hardens in about half an hour, and the hopper is again transferred relatively to the grooves in the cylinder, so as to spread the material evenly over its surface.

G. Zarniko (D. R. P. 294993, 1915; abst. J. S. C. I. 1917, **36**, 299), treats niter lime with water to decompose carbide and mixed with moist or liquid materials, to prevent dusting, in a long horizontal revolving drum, which is provided with cooling means and separate inlets for nitro-lime, liquids and inert gas, and an outlet for the finished product, which can be closed by means of a cap or valve, or may be connected with a spiral conveyer which can be made to rotate in the same, or in an opposite direction to that of the drum so as to hold back the material. Baffle plates fitted inside the

at the same time freed from dust, lime and carbide, F. MacMahan mixes commercial cyanamide with sufficient water to form a crumbling mass which is granulated and rapidly dried.¹ For the determination of N in CaCN_2 see B. Turkus.² E. Ashcroft³ has patented a method for dicyandiamide manufacture, while the Chemische Fabrik von Heyden⁴ has disclosed a process for dialkali cyanamide formation. Lead cyanamide has been described drum promote the movement of the mass in either direction. The drum is surrounded by a cooling jacket.

F. Steimmig (D. R. P. 303079, 1915; abst. J. S. C. I. 1918, **37**, 345-A) improves the physical character of crude calcium cyanamide by mixing with a dry, hydrated, neutral salt, such as sodium sulfate, free from chlorine, or with an anhydrous salt, and subsequently with a quantity of water sufficient to hydrate the salt, the mixture then being stirred until a non-dusty, friable, crystalline meal is obtained.

M. Mueller (D. R. P. 262473, 1912; abst. J. S. C. I. 1913, **32**, 920) converts crude calcium cyanamide into a fertilizer which is not dusty and but feebly caustic, by means of sulfite-cellulose waste lyes. The nitro-lime is mixed with the powdered evaporation residue of sulfate cellulose waste lyes containing about 12% of water; or completely dried evaporation residue may be used and the mixture then exposed to the air or treated in another suitable way until it has absorbed sufficient water to form a product free from carbide and showing no tendency to produce dust. (Compare A. Zamore and O. Carlson, U. S. P. 1042746, 1912; abst. J. S. C. I. 1912, **31**, 1125.)

The Nitrogen Products and Carbide Company (Jap. P. 32286, 1918; abst. C. A. 1918, **12**, 2168) treat calcium cyanamide with a small amount of water at a temperature above 60°, the reaction proceeding smoothly, without loss of ammonia; the resulting powder is then treated with 12% water and passed through rollers to obtain the granular product.

In the hydrating of commercial calcium cyanamide according to the method of B. Cooper (U. S. P. 1155797, 1915; abst. J. S. C. I. 1915, **34**, 1157) the crude material containing calcium cyanamide, oxide, and carbide, is well stirred with water or with water and oil sufficient in amount to hydrate the oxide and to decompose the carbide, the temperature being kept low to prevent the escape of ammonia. The oil serves to bind the particles of the fertilizer and does not interfere, so it is said, with the hydration.

W. Snelling, U. S. P. 1285824, 1918; abst. C. A. 1919, **13**, 251. O. Gallarder and E. Prytz, Norw. P. 28210, 1917; abst. 1919, **13**, 252. Tiniole, E. P. 121635, 1919; abst. J. S. C. I. 1919, **38**, 59-A.

1. The temperature must not be allowed to rise during the mixing with water. Granulation may be effected by forcing the mass through a sieve. Similar are the processes of G. Sinclair, U. S. P. 1278044, 1918; E. P. 15713, 1913; 105578, 1916; 9821, 1914; F. P. 474882, 1914; Can. P. 186155, 1918; abst. J. S. C. I. 1914, **33**, 933; 1915, **34**, 916, 1055; 1917, **36**, 607; 1918, **37**, 710-A; C. A. 1918, **12**, 1951, 2286. Australia P. 3105, 1917.

2. Ann. chim. anal. 1918, **23**, 3; abst. C. A. 1918, **12**, 662.

3. E. P. 16765, 1910; 25506, 1911; abst. C. A. 1913, **7**, 1590; J. S. C. I. 1911, **30**, 1211; 1913, **32**, 29; Chem. Ztg. Rep. 1913, **37**, 290. India P. 3854, 1918. Can. P. 196490, 1920. E. P. 1002, 1912; abst. C. A. 1913, **7**, 2288; J. S. C. I. 1913, **32**, 232. E. P. 10420, 1914; abst. J. S. C. I. 1915, **34**, 716. L. Radlberger, Monatsh. 1908, **29**, 937; abst. Chem. Zentr. 1908, II, 2001; Suida, Zts. physiol. chem. 1907, **50**, 174; abst. Chem. Zentr. 1907, I, 677.

4. E. P. 5051, 1913; abst. C. A. 1914, **8**, 407; J. S. C. I. 1913, **32**, 924; Chem. Ztg. Rep. 1913, **37**, 600.

by F. Bayer & Co.¹ For the continuous manufacture of calcium cyanamide, the method of C. Tofani² has received patent protection. The processes of E. and G. Polacci,³ and C. Bredig and W. Frankel,⁴ offer nothing new. C. Manuelli⁵ has determined the solubility of CaCN_2 in water.

In addition to the methods for cyanide formation previously described, may be mentioned the processes of T. Willson,⁶ A. Schweitzer and A. Hauff,⁷ P. and E. Starke,⁸ L. Devaucelle,⁹ and the Cyanid Gesellschaft.¹⁰ The latter produce nitrogen compounds from carbides¹¹ by introducing the N to be absorbed by the carbide in a direction opposite to that in which the reaction proceeds, thereby preventing the formation of molten layers of carbide. G. Erlwein¹² has reviewed in detail the various methods

1. E. P. 2140, 1912; abst. C. A. 1913, **7**, 2456; J. S. C. I. 1913, **32**, 234. E. P. 2311, 1912; abst. C. A. 1913, **7**, 2453; J. S. C. I. 1912, **31**, 900. F. P. 442004, 1912; abst. J. S. C. I. 1912, **31**, 901.
2. D. R. P. 246077; abst. J. S. C. I. 1912, **31**, 587; C. A. 1912, **6**, 2365; Chem. Zentr. 1912, **83**, I, 1646; Chem. Ztg. Rep. 1912, **36**, 292; Wag. Jahr. 1912, **58**, I, 450; Zts. ang. Chem. 1912, **25**, 1140.
3. F. P. 391693; abst. J. S. C. I. 1908, **27**, 1167; Mon. Sci. 1909, **71**, 131; Chem. Ztg. Rep. 1908, **32**, 662.
4. Belg. P. 202795. F. P. 382188; abst. J. S. C. I. 1908, **27**, 225; Mon. Sci. 1909, **71**, 102; Chem. Ztg. Rep. 1908, **32**, 108.
5. Ann. Chim. Appl. 1914, **1**, 388, 412; abst. J. S. C. I. 1914, **33**, 690.
6. "Nitrogen Compounds," U. S. P. 741396. E. P. 21755, 1895; abst. Zts. Elektrochem. 1903-1904, **10**, 274. E. P. 21997, 1895; abst. Zts. Elektrochem. 1903-1904, **10**, 275.
7. E. P. 3410, 1912; abst. C. A. 1913, **7**, 2517.
8. U. S. P. 1206155; abst. J. S. C. I. 1917, **36**, 83.
9. U. S. P. 1237485; abst. C. A. 1917, **11**, 3101; J. S. C. I. 1917, **35**, 1093. E. P. 2116, 1911; F. P. 429140; abst. J. S. C. I. 1911, **30**, 1211; 1912, **31**, 231; C. A. 1912, **6**, 1992. F. P. 478919; abst. J. S. C. I. 1916, **35**, 1109.
10. D. R. P. 228925, 1907; abst. Mon. Sci. 1914, **81**, 86; Chem. Zentr. 1911, **82**, I, 49; Chem. Ztg. Rep. 1910, **34**, 632; Chem. Zts. 1911, **10**, No. 2238; Wag. Jahr. 1910, **56**, I, 517; Zts. ang. Chem. 1910, **23**, 87. Addn. to D. R. P. 227854; abst. C. A. 1911, **5**, 2160; Mon. Sci. 1915, **82**, 53; Chem. Zentr. 1910, **81**, II, 1577; Chem. Ztg. Rep. 1910, **34**, 569; Chem. Zts. 1910, **9**, No. 2124; Jahr. Chem. 1910, **63**, I, 551; Wag. Jahr. 1910, **56**, I, 516; Zts. ang. Chem. 1910, **23**, 2338. D. R. P. 203308; abst. J. S. C. I. 1908, **27**, 1204; Mon. Sci. 1911, **75**, 161; Chem. Zentr. 1908, **79**, II, 1657; Chem. Ztg. Rep. 1908, **32**, 609; Chem. Zts. 1909, **8**, No. 1198; Jahr. Chem. 1905-1908, **1**, 2059; Wag. Jahr. 1908, **54**, I, 467; Zts. ang. Chem. 1909, **22**, 270. F. P. 382743, first addn. dated Oct. 11, 1907; second addn. dated Oct. 12, 1907; Mon. Sci. 1909, **71**, 103; Chem. Ztg. Rep. 1908, **32**, 129, 146. F. P. 328031, 1902; abst. J. S. C. I. 1903, **22**, 1194. E. P. 16298, 1902; abst. J. S. C. I. 1903, **22**, 554; Chem. Ztg. 1903, **27**, 1180. J. S. C. I. 1908, **27**, 281. Zts. ang. Chem. 1902, **16**, 520.
11. D. R. P. 227854; abst. Mon. Sci. 1915, **82**, 53; Chem. Zentr. 1910, **81**, II, 1577; Chem. Ztg. Rep. 1910, **34**, 569; Chem. Zts. 1910, **9**, No. 2124; Jahr. Chem. 1910, **63**, I, 551; Wag. Jahr. 1910, **56**, I, 516; Zts. ang. Chem. 1910, **23**, 2338.
12. Zts. Elektrochem. 1906, **12**, 551; abst. Jahr. Chem. 1905-1908, I, 2432.

for nitride formation, and has analyzed them critically.

The next step after cyanamide formation is transformation into ammonia, which in turn is readily oxidized to nitric acid by the methods previously described. The usual method¹ is to heat calcium cyanamide, or nitrogen compounds prepared from it, such as cyanamide or dicyanodiamide, with water and an alkaline hydrate or carbonate. The calcium cyanamide may be heated with the alkali solution, or treated with carbon dioxide and then lixiviated, or may be lixiviated and the solution treated with CO₂ to obtain cyanamide or dicyanodiamide.² The processes of P. Weber,³ E. Naef,⁴ W. Phillips and J. Bulteel,⁵ J. Bucher,⁶ B. Hansen,⁷ C. Thorssell,⁸ N. Tommasi,⁹ and H. Mehner,¹⁰ being modifications of this general method of ammonia formation.

If the formation of calcium nitrate is desired, the methods of A. Schloesing,¹¹ E. Collett and M. Eckardt,¹² and H. Ditz and

1. E. P. 18207, 1911; abst. J. S. C. I. 1911, **30**, 1252; C. A. 1913, **7**, 404.
2. W. Hale and F. Vibrans, J. A. C. S. 1918, **40**, 1046; abst. J. S. C. I. 1918, **37**, 522-A.
3. E. P. 445506; abst. J. S. C. I. 1913, **32**, 23.
4. E. P. 14412, 1912; abst. C. A. 1913, **7**, 4050; J. S. C. I. 1913, **32**, 424; Chem. Ztg. Rep. 1913, **37**, 634.
5. E. P. 23046, 1910; abst. C. A. 1912, **6**, 1591; J. S. C. I. 1911, **30**, 1252; Chem. Ztg. Rep. 1912, **36**, 170.
6. E. P. 23292, 1914; abst. J. S. C. I. 1916, **35**, 46.
7. U. S. P. 1205619; abst. J. S. C. I. 1917, **36**, 24.
8. E. P. 11485, 1915; abst. J. S. C. I. 1915, **34**, 1207. "Production of ammonia by heating barium cyanide with water in an autoclave," E. P. 11486, 1915; abst. J. S. C. I. 1916, **35**, 963.
9. E. P. 476294, 1914; abst. J. S. C. I. 1916, **35**, 46; U. S. P. 1230343, 1917; abst. J. S. C. I. 1917, **36**, 872. See also Cie. pour la Fabrication des Compteurs et Material d'Usines a Gaz. E. P. 407164; abst. J. S. C. I. 1910, **29**, 565; Mon. Sci. 1910, **73**, 175. Akt. Ges. f. Stickstoffdünger, E. P. 2407, 1907. E. P. 375979; abst. J. S. C. I. 1907, **26**, 925; Mon. Sci. 1908, **69**, 86. E. P. 450435; abst. Chem. Ztg. 1913, **37**, 244. U. S. P. 922003. D. R. P. 163320, 1901; abst. Zts. ang. Chem. 1905, **18**, 1909; Mon. Sci. 1906, **65**, 149; 1915, **82**, 14; Chem. Centr. 1905, **76**, II, 1059; Chem. Ztg. 1905, **29**, 1089; Chem. Zts. 1906, **5**, 58; Jahr. Chem. 1905-1908, I, 2433, 2435; Wag. Jahr. 1905, **51**, I, 489; Zts. ang. Chem. 1905, **18**, 1909.
10. E. P. 28667, 1903; abst. J. S. C. I. 1905, **24**, 132.
11. U. S. P. 1177359; abst. C. A. 1916, **10**, 1582; J. S. C. I. 1916, **35**, 539. See also C. A. 1915, **9**, 849. For methods of pulverizing calcium nitrate without the formation of dust, see E. P. 466963, 1914; abst. J. S. C. I. 1914, **33**, 865. E. P. 468, 1914; abst. J. S. C. I. 1914, **33**, 1154. Swiss P. 77376, 1918; abst. C. A. 1918, **12**, 2113.
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F. Kanhäuser are applicable¹ in especial instances.

• Besides its value as a fertilizer and the source of ammonia, it is used in the production of cyanides, guanidine, thiourea and veronal. By the interaction of cyanamide and nitric acid in concentrated solution below 20°, urea nitrate is precipitated almost quantitatively.²

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2. Oest. Ver. f. Chem. u. metall. Produktion, D. R. P. 285259, 1914; abst. J. S. C. I. 1915, **34**, 1166.

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Other Processes for the Catalytic Production of Ammonia.

In addition to the Haber, Badische and Ostwald processes al-

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to the manufacturing stage on a sound economic footing, but which merit attention.

A. Classen¹ subjects nitrogen and hydrogen to the simultaneous action of silent and spark electric discharges in presence of catalysts, e. g., metals and metallic alloys, supported on carriers of an acidic nature. Silica, prepared from water-glass, is well suited for this purpose, as it readily absorbs colloidal metals such as gold, platinum, metals of the platinum and iron groups, as well as their alloys. The efficiency of the catalyst is improved by the presence of a protective colloid, e. g., gelatose. The mixed gases are passed over the catalyst between two electrodes, one being a good conductor, like copper, and the other a bad conductor, like glass or porcelain. The latter may be immersed in cold water and may concentrically surround the former, the contact material being in the intervening space. The temperature may range from 25° to 90°, according to the conditions, and the pressure may be normal or increased.

The Berlin Anhaltische Maschinenbau Akt.² combine for the production of nitrogen oxides from ammonia by catalysts, conduits for the ammonia gas and the air, which are connected with each other in a fixed way, allowing the gases to be continually

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2. D. R. P. 286991; abst. J. S. C. I. 1916, **35**, 116; Chem. Zentr. 1917, **88** I 729; Chem. Ztg. Rep. 1915, **39**, 406; Zts. ang. Chem. 1915, **28**, 521.

mixed in any proportion before they pass on to the chambers containing the catalyst. The processes of B. Aubertin,¹ W. Landis,² K. Kaiser,³ Elektrochemische Werke Ges.,⁴ F. Bensa,⁵ A. Frank,⁶ P. Hershman,⁷ S. Barth⁸ and W. Schmidt⁹ are similar to the above.

According to the process of A. Wells¹⁰ nitrogen oxides are formed from ammonia by passing a mixture of ammonia and air through catalytic chambers. The surfaces with which the gases come into contact with a catalyst, e. g., platinum, nickel or cobalt vanadate or tin chromate and an inert carrier. The chambers are heated, preferably to a temperature of about 500°-700°, and heat interchanged is effected between the oxidation products and the gases entering the catalytic chamber.

F. Washburn¹¹ adds free ammonia to a solution of nitric acid to form ammonium nitrate, which is recovered and added to concentrated sulfuric acid to form a strong nitric acid. According to the Badische Anilin and Soda Fabrik,¹² better yields of ammonia are obtained in the synthetic process if a promoter is added to the catalyst other than iron, cobalt and nickel while excluding contact poison. Oxides or other suitable compounds of the alkali and alkaline-earth metals, earth metals, the rare-earth metals, and also tantalum and niobium are suitable as promoters, while

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2. U. S. P. 1173524; abst. J. S. C. I. 1916, **35**, 468.
3. E. P. 24035, 1911; abst. C. A. 1913, **7**, 1405; J. S. C. I. 1912, **31**, 775. Aust. P. 48323, 1911. Chem. Ztg. Rep. 1916, **40**, 112; abst. C. A. 1916, **10**, 1080. See also C. A. 1916, **10**, 806; J. S. C. I. 1912, **31**, 385.
4. E. P. 5282, 1911; abst. J. S. C. I. 1912, **31**, 231. F. P. 426307, 1911; abst. J. S. C. I. 1911, **30**, 1012; Mon. Sci. 1913, **79**, 122.
5. E. P. Appl. 11036, 1915; abst. J. S. C. I. 1916, **35**, 51.
6. D. R. P. 224329; abst. C. A. 1910, **4**, 3125; Chem. Zentr. 1910, **81**, 11, 511; Chem. Ztg. Rep. 1910, **34**, 397; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 485; Zts. ang. Chem. 1910, **23**, 2098; Zts. Schiess. Spreng. 1910, **5**, 338.
7. Can. P. 175749, 175750, 1917; abst. C. A. 1917, **11**, 3103.
8. Swiss P. 73377, 1916; abst. C. A. 1917, **11**, 193.
9. U. S. P. 1252726; abst. C. A. 1918, **12**, 657; J. S. C. I. 1918, **37**, 149-A.
10. U. S. P. 1252976; abst. C. A. 1918, **12**, 747; J. S. C. I. 1918, **37**, 148-A.
11. U. S. P. 1206062, 1206063, 1217247; abst. J. S. C. I. 1917, **36**, 83, 503; C. A. 1917, **11**, 191, 1526. Can. P. 173159, 1916; abst. C. A. 1918, **12**, 205.
12. E. P. 5835, 1911; abst. C. A. 1912, **6**, 2500; J. S. C. I. 1911, **30**, 1115. See also E. P. 10441, 10249, 1910; F. P. 416877, 425099; abst. J. S. C. I. 1910, **29**, 1378; 1911, **30**, 87, 1012, 1116; C. A. 1912, **6**, 1346; Chem. Ztg. Rep. 1911, **35**, 575.

contact poisons include the metalloids such as sulfur, selenium, tellurium, arsenic, phosphorus, and also the easily fusible and at the same time easily reducible metals such as lead and tin. The effect of the addition of any body is determined by making a comparative test with a portion of the catalyst that has not been treated. It is found generally that compounds of those metals that yield non-reducible oxides and salts are suitable as promoters, when used in conjunction with catalysts such as the alkali or alkaline-earth metals, the earth metals, manganese, tungsten, molybdenum, osmium and the noble metals. The gases themselves are freed from contact poison by passage over a material capable of absorbing it; conveniently a further portion of the catalyst placed in advance. In examples, ammonia is prepared by the passage of nitrogen over a mixture of cerium and potassium nitrate, a mixture of osmium oxide hydrate and potassium osmate which has been reduced in hydrogen, a mixture of barium and potassium nitrate, or lithium, calcium or aluminium either the form of metal or as nitride, amide, hydride or carbide, may replace the barium, a mixture of potassium oxide and an alloy of mercury and manganese, the whole being heated until the mercury has distilled off. Meister, Lucius and Bruening¹ and also Rohmer² burn a homogeneous mixture of ammonia and air, containing about 10%–14½% NH₃, and only sufficient oxygen required for the oxidation of ammonia into the desired nitrogen oxides, in the presence of a platinum-asbestos catalyzer. In another process,³ the mixture of air and ammonia is forced through the catalyzer at a pressure greater than normal atmospheric, by means of a perforated disc placed behind the catalyst. The processes of C. Ellis,⁴ Chemische Fabrik Griesheim-Elektron,⁵ Pease,⁶ A. Wells,⁷ Verein

1. E. P. 3662, 28737, 1913; abst. C. A. 1914, **8**, 2607; J. S. C. I. 1913, **32**, 1011; 1914, **33**, 483. F. P. 453845. D. R. P. 286751, 289562, 289563; abst. Chem. Zentr. 1916, **87**, I, 192; 1917, **88**, I, 638; Chem. Ztg. Rep. 1915, **39**, 357; 1916, **40**, 48; Zts. ang. Chem. 1915, **28**, 508; 1916, **29**, 69.

2. U. S. P. 1096392, 1096393; abst. C. A. 1914, **8**, 2228; Mon. Sci. 1914, **81**, 137.

3. Verein Chemischer Fabriken, Mannheim, E. P. 12600, 1914; abst. J. S. C. I. 1915, **34**, 962; C. A. 1915, **9**, 3120. F. P. 472567; abst. J. S. C. I. 1915, **34**, 492.

4. U. S. P. 1233561, 1237884; abst. C. A. 1917, **11**, 2602, 3102; J. S. C. I. 1917, **36**, 1007, 1094.

5. Aust. P. 34031, 1908.

6. E. P. Appl. 1053, 1918; abst. J. S. C. I. 1918, **37**, 79-A.

7. U. S. P. 1252976; abst. C. A. 1918, **12**, 747; J. S. C. I. 1918, **37**, 148-A.

Chemischer Fabriken in Mannheim,¹ M. Pier,² J. Price,³ and C. Bosch, A. Mittasch and C. Beck,⁴ are similar.

The Farbwerke vorm. Meister, Lucius u. Brueuning⁵ have shown that nitrogen and nitrogen oxides are alone produced by the combustion of ammonia in air in the presence of contact agents by employing such an amount of ammonia that there is no excess of oxygen in the reacting mixture, while the oxygen is present in a quantity just sufficient for the production of higher or lower oxides. The nitrogen oxides may be condensed with the water present forming nitric acid, or by suitable adjustment sodium nitrite may be obtained by treating the gases with caustic soda lye. Or the process may be arranged so that nitric oxide is the only oxide produced from which the water present may be separated by cooling, and air afterwards admitted to oxidize the nitric oxide, the resulting oxides being separated from the nitrogen in the further cooling and absorbing apparatus. The apparatus used consists of an iron tube containing platinized asbestos or several diaphragms of wire netting, or a finely perforated platinum sheet, or a narrow tube of platinum or the like.

In the process of the Elektrizitätswerk Lonza,⁶ air is allowed to flow through a solution of ammonium sulfate in countercurrent at a temperature of 70°–75°, the ammonia formed by hydrolysis being separated from the nitrogen. F. Naumann,⁷ P. Fox,⁸ operate similarly. C. Ellis⁹ produces nitrogen oxides employing silver

1. E. P. 12600, 1914; abst. C. A. 1915, **9**, 3120; J. S. C. I. 1915, **34**, 962.
2. E. P. 213, 214, 9661, 1914; 100216, 100470; abst. J. S. C. I. 1915, **34**, 870; 1916, **35**, 538, 737. U. S. P. 1090874, 1119534, 1157253, 1159865; abst. C. A. 1914, **8**, 1856; J. S. C. I. 1914, **33**, 485; 1915, **34**, 1250; Mon. Sci. 1914, **81**, 99; 1915, **82**, 18; 1916, **83**, 37; Chem. Ztg. Rep. 1914, **38**, 499; 1915, **39**, 282; Zts. ang. Chem. 1916, **29**, I, 133. D. R. P. 252997; abst. C. A. 1913, **7**, 541; Chem. Zentr. 1912, **83**, II, 1755; Chem. Ztg. Rep. 1912, **36**, 618; Wag. Jahr. 1912, **58**, I, 386; Zts. ang. Chem. 1912, **25**, 2505.
3. E. P. 10755, 1909; abst. C. A. 1911, **5**, 2312.
4. U. S. P. 1207706, 1207707, 1207708; abst. C. A. 1917, **11**, 278; J. S. C. I. 1917, **36**, 84.
5. E. P. 3662, 1913; abst. C. A. 1914, **8**, 2607; J. S. C. I. 1913, **32**, 1011. D. R. P. 289503. Addn. to D. R. P. 286751; abst. C. A. 1916, **10**, 1412, 2620; Chem. Zentr. 1917, **88**, I, 638; Chem. Ztg. Rep. 1915, **39**, 357; Zts. ang. Chem. 1915, **28**, 508.
6. Swiss P. 73378, 1916; abst. C. A. 1917, **11**, 193.
7. D. R. P. 259995; abst. C. A. 1913, **7**, 3001; Chem. Zentr. 1913, **84**, I, 2009; Chem. Ztg. Rep. 1913, **37**, 282; Wag. Jahr. 1913, **59**, I, 396; Zts. ang. Chem. 1913, **26**, 347.
8. J. Ind. Chem. 1917, **9**, 737; abst. C. A. 1917, **11**, 2178.
9. U. S. P. 1237884; abst. C. A. 1917, **11**, 3102; J. S. C. I. 1917, **35**, 1094.

molybdate, vanadate or phosphate, or silver manganese chromate as catalysts. The oxidation of ammonia by air is effected by the Verein Chem. Fabr. Mannheim,¹ by forcing the mixture through the catalyst so that the pressure of the products is above that of the atmosphere. This may be brought about by a porous plate after the catalyst. E. Herman² burns methane with air enriched with oxygen under high pressure or causes it to undergo flameless combustion by contact with a mass of zircon. A yield of 3%–4% by volume of oxides of nitrogen is claimed with a consumption of about 2.5 cubic meters methane per kilo 100% nitric acid. The Badische Anilin und Soda Fabrik³ employs a catalyst of the iron group and an oxide of bismuth to oxidize ammonia by air. The claim also covers the replacement of either of the above by an oxide of a rare earth or a mixture of three or more such materials. The binding material should not contain a large amount of non-metals or their compounds, a yield of 90% oxides of nitrogen is said to be produced. It is suggested to dissolve fifteen parts of nitrate of iron with one part of lanthanum nitrate in water and precipitate by ammonia. The lumps are dried at 250° C., heated to 600° C., and used at 700° C.

In the process of F. Ilavati⁴ ammonia and other nitrogen-hydrogen compounds, such as hydrazine and hydroxylamine, are prepared synthetically by ionizing by electric discharges a mixture of, or containing, nitrogen and hydrogen, and then passing the gases over a catalyst consisting of a mixture of a metal of the platinum group and titanium in a finely divided state and supported on an indifferent substance such as asbestos or tufa. The metals in the catalyst are preferably mixed in the proportion of their atomic weights. In a modification, the catalyst is

1. F. P. 472567; abst. J. S. C. I. 1915, **34**, 492.

2. D. R. P. 281084; abst. J. S. C. I. 1915, **34**, 613; Mon. Sci. 1917, **84**, 75; Chem. Zentr. 1915, **86**, I, 176; Chem. Ztg. Rep. 1915, **39**, 14; Zts. ang. Chem. 1915, **28**, 82.

3. E. P. 13687, 13848, 1914; abst. J. S. C. I. 1915, **34**, 799, 961. See N. Caro, D. R. P. 272638; abst. J. S. C. I. 1914, **33**, 593; C. A. 1914, **8**, 2467; Chem. Zentr. 1914, **85**, I, 1614; Chem. Ztg. Rep. 1914, **38**, 237; Wag. Jahr. 1914, **60**, I, 310; Zts. ang. Chem. 1914, **27**, 303. N. Caro, Zts. ang. Chem. 1909, **22**, 1178; 1910, **23**, 2412; 1911, **24**, 505.

4. E. P. 1142, 1913; abst. C. A. 1914, **8**, 2461; J. S. C. I. 1913, **32**, 911. U. S. P. 1079705; abst. C. A. 1914, **8**, 405; Mon. Sci. 1914, **81**, 27. D. R. P. 275663, 277054; abst. Chem. Zentr. 1914, **85**, II, 276, 596; Chem. Ztg. Rep. 1914, **38**, 404, 466; Wag. Jahr. 1914, **60**, I, 309, 451; Zts. ang. Chem. 1914, **27**, 480, 564. Aust. P. 72211; abst. J. S. C. I. 1914, **33**, 1009, 1154; C. A. 1917, **11**, 874.

rendered active by the emanation from pitchblende or other radio-active material, in which case the ionizing treatment may be wholly or in part dispensed with. In carrying out the process the gases are ionized by passage through a spark or brush discharge, and are cooled before passing over the catalyst contained in chambers or tubes. The gases are cooled when passing from chamber to chamber until a temperature is reached at which the gases are absorbed by the catalyst. The rise of temperature consequent on absorption sets free the gases in a nascent state when they combine to form ammonia. Too great a rise in temperature is avoided by employing gases under pressure and sprinkling the chambers with water. If oxygen or water-vapor is present in the gases, compounds with the catalyst are formed. These are decomposed by increasing the temperature and reducing the pressure, after which the gas may be again conducted over the catalyst but in reverse direction. If two or more sets of apparatus are available, a continuous production may be arranged for.

A. Lymn¹ obtains ammonium nitrite or nitrate by oxidizing ammonia in producer gas by means of nitrogen oxides. Another process² treats the ammoniacal gases obtained from lime-nitrogen with caustic alkalis or alkaline earths before their catalytic oxidation, in order to render innocuous the silicon hydride, phosphorus hydride and acetylene, brought in as impurities by the lime-nitrogen, which otherwise cover the catalyzer (platinum) with a layer consisting principally of silica, and soon render it inactive.

The processes of E. Monckton,³ H. Lamb,⁴ W. Feld,⁵ and E. Collett and M. Eckardt⁶ offer but little that is new. C. Parsons⁷

1. E. P. 1851, 1913; abst. C. A. 1914, **8**, 2462; J. S. C. I. 1914, **33**, 244. F. P. 467592; abst. Mon. Sci. 1916, **83**, 15.

2. The "Oesterreichische Verein für Chem. und Metallurgische" production at Aussig, D. R. P. 251934, 276720; abst. C. A. 1913, **7**, 405; Chem. Zentr. 1912, **83**, II, 1502; 1914, **85**, II, 551; Chem. Ztg. Rep. 1912, **36**, 607; 1914, **38**, 466; Wag. Jahr. 1912, **58**, I, 387; 1914, **60**, I, 310; Zts. ang. Chem. 1912, **25**, 2378; 1914, **27**, 565. Aust. Appl. A-9851; abst. J. S. C. I. 1912, **31**, 1125; 1915, **34**, 28.

3. E. P. 1890, 1869. E. P. 265, 3509, 1874.

4. U. S. P. 1207567; abst. J. S. C. I. 1917, **36**, 83.

5. E. P. 5838, 1911; abst. C. A. 1912, **6**, 2517; J. S. C. I. 1912, **31**, 490.

6. E. P. 5713, 1911; C. A. 1912, **6**, 2501; J. S. C. I. 1911, **30**, 1058. A. Hiorth, Norw. 27386, 1916; abst. C. A. 1917, **11**, 278.

7. U. S. P. 1239125; abst. C. A. 1917, **11**, 3394; J. S. C. I. 1917, **35**,

has "dedicated to the public" a process whereby nitrogen oxides are formed by passing a mixture of ammonia and oxygen containing gas over a catalyst formed of lead oxide or lead chromate and a carrier of bone ash or other material not reactive with the lead chromate or the lead oxide at a temperature of 1000°. Crystal aluminium oxide or carborundum may serve as carriers for the lead compounds as well as bone ash. The patent is dedicated to the public for free employment without payment of any royalty.

P. Starke has outlined a process¹ whereby a catalytic mass is prepared by mixing sodium carbonate 20, magnesium oxide 30, and metallic iron 50 parts, with or without the addition of carbon or crude oil or molasses to increase the porosity of the mass, grinding this mixture thoroughly and heating it to 400°–800°. Ammonia is then produced by passing through the catalytic mass, a mixture of air and natural gas 14 parts at a temperature below that at which cyanides are formed. The temperature and pressure may vary widely, a higher pressure rendering possible working at a lower temperature and conversely. A temperature of 600° and a pressure of 200 atmospheres is stated to have given the best yields of ammonia. Nickel, cobalt, chromium, aluminium or oxides or salts of iron may replace iron as an ingredient of the catalytic mixture. According to Donath and Indra, ammonia may be transformed into nitric acid in the following ways:

1. Oxidation of gaseous ammonia, with or without addition of air, by chemical means, by substances giving off oxygen at higher temperatures.
2. Oxidation of gaseous ammonia by atmospheric oxygen at higher temperatures with the assistance of catalyzers.
3. Oxidation of aqueous solutions of ammonia, therefore at comparatively low temperatures, by substances giving off oxygen.
4. Electrolytic oxidation of ammonia solutions.
5. Bacterial nitrification of ammonia.

L. Summers,² C. Stuart-Bailey,³ The Nordyke & Marmon

1127. See C. Parsons and L. Jones, E. P. 132551, 136342, 1918. U. S. P. 1321376; abst. J. S. C. I. 1919, **38**, 817-A; 1920, **39**, 23-A.

1. U. S. P. 1256273; abst. C. A. 1918, **12**, 981; J. S. C. I. 1918, **37**, 241-A.

2. U. S. P. 1242264; abst. C. A. 1918, **12**, 121; J. S. C. I. 1917, **36**, 1235.

3. E. P. 19189, 1905; abst. J. S. C. I. 1906, **25**, 1044; Chem. Ztg. Rep. 1907, **31**, 72.

Co.,¹ R. Marston,² F. Bayer & Co.,³ Chemische Fabrik Griesheim-Elektron,⁴ K. Kaiser,⁵ A. Frank and N. Caro,⁶ M. Wendriner,⁷ D. Meneghini,⁸ Oest. Verein f. Chem. u. Metall. Produktion,⁹ W. Reinders and A. Cats,¹⁰ L. Jones, D. Morton, G. Terziev and Semet Solvay Co.,¹¹ and A. Montbaron and A. Ducommun-Mueller¹² have also patented refinements on the general principles as laid down by Haber, the Badische and Ostwald.

For the theoretical aspects of the problem and the advancements, especially from the electrical engineering point of view, the work of W. Weith,¹³ Siemens & Halske,¹⁴ J. Liebig,¹⁵ O. Michel

1. D. R. P. 189472; abst. Chem. Zentr. 1907, **78**, II, 1951; Chem. Ztg. Rep. 1907, **31**, 549; Chem. Zts. 1907, **6**, No. 406; Jahr. Chem. 1905-1908, I, 1779; Wag. Jahr. 1907, **53**, I, 409; Zts. ang. Chem. 1908, **21**, 797. E. P. 1204, 1906; abst. J. S. C. I. 1906, **25**, 536. F. P. 362434.

2. E. P. 19074, 1900; abst. J. S. C. I. 1901, **20**, 1209; Chem. Ztg. 1902, **26**, 206.

3. U. S. P. 763491; abst. Mon. Sci. 1904, **61**, 142; Chem. Zts. 1904, **3**, 692. E. P. 18594, 1903; abst. J. S. C. I. 1904, **23**, 787. D. R. P. 168272; abst. Chem. Centr. 1906, **77**, I, 1198; Chem. Ztg. 1906, **30**, 425; Chem. Zts. 1906, **5**, 344; Jahr. Chem. 1905-1908, I, 1777; Wag. Jahr. 1906, **52**, I, 449; Zts. ang. Chem. 1906, **19**, 1941; Zts. Schiess. Spreng. 1906, **1**, 103. F. P. 335229; abst. J. S. C. I. 1904, **23**, 186; Chem. Ztg. 1905, **29**, 531; Mon. Sci. 1904, **61**, 75.

4. E. P. 13954, 1907; abst. J. S. C. I. 1908, **27**, 447. F. P. 380884. U. S. P. 971149; abst. Mon. Sci. 1913, **79**, 100; Chem. Ztg. Rep. 1910, **34**, 610. D. R. P. Ann. C. 17336.

5. U. S. P. 987375; abst. Mon. Sci. 1911, **75**, 114; Chem. Ztg. Rep. 1911, **35**, 248. E. P. 20325, 1910; abst. J. S. C. I. 1910, **29**, 1377; Chem. Ztg. Rep. 1911, **35**, 3. F. P. 419782; abst. J. S. C. I. 1911, **30**, 130; Mon. Sci. 1913, **79**, 88. D. R. P. Ann. 42005.

6. D. R. P. 224329; abst. Chem. Zentr. 1910, **81**, II, 511; Chem. Ztg. Rep. 1910, **34**, 397; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 485; Zts. ang. Chem. 1910, **23**, 2098; Zts. Schiess. Spreng. 1910, **5**, 338. Bayerische Stickstoffwerke A. G., D. R. P. 236705; abst. Chem. Zentr. 1911; **82**, II, 315; Chem. Ztg. Rep. 1911, **35**, 392; Wag. Jahr. 1911, **57**, I, 429; Zts. ang. Chem. 1911, **24**, 1495.

7. Chem. Ind. 1911, **34**, 456. W. Feld, Belg. 174934, 1904; 188779, 1905; 204664, 204696, 204719, 1907.

8. Gazz. chim. ital. 1912, **42**, 126; J. S. C. I. 1912, **31**, 383.

9. Aust. Ann. A 9851. F. Dafert and R. Miklauz, E. P. 16597, 1914; abst. J. S. C. I. 1915, **34**, 871; Chem. Ztg. Rep. 1916, **40**, 146. F. P. 474994; abst. Mon. Sci. 1916, **83**, 83.

10. Chem. Weekblad, **9**, 47; abst. C. A. 1912, **6**, 3234; Chem. Zentr. 1912, **83**, I, 708.

11. U. S. P. 1037261; abst. C. A. 1912, **6**, 3498; J. S. C. I. 1912, **31**, 922; Mon. Sci. 1913, **79**, 5; Chem. Ztg. Rep. 1913, **37**, 32.

12. F. P. 400805; abst. Mon. Sci. 1911, **75**, 149. G. Calvert, E. P. 10612, 1914; abst. J. S. C. I. 1915, **34**, 715.

13. Ber. 1874, **7**, 1745.

14. D. R. P. 85103; F. P. 335453; abst. J. S. C. I. 1904, **23**, 193; Chem. Ind. 1896, **19**, 186, 387; Zts. ang. Chem. 1896, **9**, 75; Mon. Sci. 1896, **47**, 72; 1904, **61**, 76; Ber. 1897, **29**, 245; Chem. Centr. 1896, **67**, I, 1216; Chem. Ztg. 1896, **20**, 204; Jahr. Chem. 1896, **49**, 414; Wag. Jahr. 1896, **42**, 410; Zts. ang. Chem. 1896, **9**, 75.

15. Mag. Pharm. **33**, 40. See also: R. Koepp & Co., E. P. 30073,

and E. Grandmougin,¹ E. Donath and A. Indra,² F. Kuhlmann,³ E. Donath,⁴ W. Kochmann,⁵ G. Oesterheld,⁶ D. Meneghini,⁷ M. Herschkowitsch,⁸ N. Smith,⁹ F. Sestini,¹⁰ R. Kempf,¹¹ M. Levi and E. Migliorini,¹² W. Traube and A. Biltz,¹³ O. Loew,¹⁴ E. Andersen,¹⁵ F. Fichter and H. Kappeler,¹⁶ F. Fichter,¹⁷ F. Müller,¹⁸ A. Millot,¹⁹ A. Brochet and G. Boiteau,²⁰ G. Scagliarini and A. Casali,²¹

1913; U. S. P. 1098139; abst. J. S. C. I. 1914, **33**, 788; 1916, **35**, 738. E. P. 22225, 1905; U. S. P. 802980; abst. J. S. C. I. 1905, **24**, 1254; 1906, **25**, 495. Belg. P. 263473, 1913. A. Matignon, U. S. P. 1089240, 1089241; abst. C. A. 1914, **8**, 1490; Mon. Sci. 1914, **81**, 97; Chem. Ztg. Rep. 1914, **38**, 261; Zts. ang. Chem. 1915, **28**, I, 205. F. P. 430595; abst. C. A. 1912, **6**, 2149; Mon. Sci. 1913, **79**, 127; Chem. Ztg. Rep. 1912, **36**, 57; J. S. C. I. 1911, **32**, 1211. H. Castner, E. P. 12218, 1894; abst. J. S. C. I. 1895, **14**, 572; Chem. Centr. 1895, **66**, II, 699.

1. Ber. 1893, **26**, 2565. A. Nodon, D. R. P. 274346; abst. C. A. 1914, **8**, 2851; Chem. Zentr. 1914, **85**, II, 94; Chem. Ztg. Rep. 1914, **38**, 323; Wag. Jahr. 1914, **60**, I, 356; Zts. ang. Chem. 1914, **27**, 397.

2. "Die Oxydation des Ammoniaks zu Salpetersäure und Salpetriger Säure," 1913; abst. C. A. 1913, **7**, 2456. B. Lepsius, F. P. 466102; abst. J. S. C. I. 1914, **33**, 644; C. A. 1914, **8**, 3492; Chem. Ztg. Rep. 1914, **38**, 579.

3. Ann. 1841, **39**, 319; J. pr. Chem. 1841, **24**, 225.

4. Zts. Schiess. Spreng. 1916, **11**, 170.

5. Arb. d. pharm. Inst. Berlin, 1911. H. Koppers, D. R. P. 285354; abst. J. S. C. I. 1915, **34**, 1142. Belg. P. 186040, 1905; 218474, 1909; abst. Chem. Zts. 1905, **5**, 343.

6. Zts. anorg. Chem. 1914, **86**, 103.

7. Gazz. chim. ital. 1912, **42**, 126; **43**, I, 81; J. S. C. I. 1912, **31**, 383; 1913, **32**, 230.

8. Zts. Phys. Chem. 1909, **65**, 93; Chem. Zentr. 1909, **80**, I, 256.

9. J. C. S. 1906, **89**, 473. Nobel's Explosives Co. and D. Cross, E. P. 24607, 1910; 9682, 1911; abst. C. A. 1912, **6**, 1406; J. S. C. I. 1911, **30**, 1211.

10. Zts. ang. Chem. 1904, **17**, 1380; 1905, **18**, 823.

11. Ber. 1905, **38**, 3966. H. Mehner, U. S. P. 607943; D. R. P. 88999, 92810; abst. Zts. ang. Chem. 1896, **9**, 470; 1897, **10**, 405; Chem. Centr. 1897, **68**, I, 142; II, 880; Chem. Ztg. 1896, **20**, 934; 1897, **21**, 619; Jahr. Chem. 1897, **50**, 529; Wag. Jahr. 1896, **42**, 411; 1897, **43**, 442. E. P. 12471, 1895; abst. J. S. C. I. 1896, **15**, 544.

12. Gazz. chim. ital. 1908, **38**, ii, 10.

13. Ber. 1904, **37**, 3130; 1906, **39**, 166.

14. J. prakt. Chem. 1879, **126**, 298.

15. Zts. Elektrochem. 1916, **23**, 441; abst. J. S. C. I. 1917, **36**, 81. P. Lepsius, Belg. P. 262919, 1913. A. Lyman, Belg. P. 256412, 1913.

16. Zts. Electrochem. 1912, **18**, 647. E. Jolicard, Belg. P. 261193, 1913. J. Jackson, Belg. P. 260381, 1913.

17. Chem. Ztg. 1912, **36**, 606.

18. Chem. Zentr. 1911, **82**, I, 626. R. Wallace and E. Wasmer, U. S. P. 1083232; E. P. 18450, 1912; F. P. 434692; abst. J. S. C. I. 1914, **33**, 22; C. A. 1914, **8**, 556, 1192; Mon. Sci. 1914, **81**, 65; 1916, **83**, 12; Chem. Ztg. Rep. 1914, **38**, 457.

19. Bull. Soc. Chim. 1887, (2), **48**, 610. A. Kroll, Belg. P. 234643, 1911.

20. Bull. Soc. Chim. 1909, (4), **5**, 667.

21. Chem. Zentr. 1913, **84**, I, 994. A. Serret, F. P. 462633; abst. J. S. C. I. 1914, **33**, 312.

W. Moldenhauer,¹ G. Scagliarini,² O. Dieffenbach,³ O. Uhde,⁴ H. Kaserer,⁵ E. Muller and F. Spitzer,⁶ Besson and Rosset,⁷ O. Böcker and R. Schmidt,⁸ A. Brochet and G. Boiteau,⁹ G. Bourgerel,¹⁰ F. Haber,¹¹ F. Klinkerfues,¹² G. Taylor and J. Capps,¹³ A. D.,¹⁴ E. Maxted,¹⁵ E. Donath,¹⁶ and A. Crosby¹⁷ should be

1. Zts. ang. Chem. 1914, **27**, I, 334.
2. Gaz. chim. ital. 1913, **43**, I, 30; 1914, **44**, I, 543; abst. Chem. Zentr. 1913, **84**, I, 1263; 1914, **85**, II, 1024.
3. Chem. Ind. 1914, **37**, 265. T. Winstanley and F. Williams, E. P. 21304, 1912; abst. J. S. C. I. 1912, **33**, 1009; C. A. 1914, **8**, 995; Chem. Ztg. Rep. 1913, **37**, 697.
4. Chem. Ztg. 1914, **38**, 1015.
5. Zts. landw. Vers. Wes. Öst. **10**, 37; abst. Chem. Zentr. 1907, **78**, I, 652. J. Wolf, D. R. P. 281317; abst. J. S. C. I. 1915, **34**, 612; Mon. Sci. 1917, **84**, 75; Chem. Zentr. 1915, **86**, I, 229; Chem. Ztg. Rep. 1914, **38**, 14; Wag. Jahr. 1914, **60**, I, 309; Zts. ang. Chem. 1915, **28**, 81.
6. Zts. Electrochem. 1905, **11**, 917; abst. Chem. Centr. 1905, **76**, II, 808.
7. Compt. rend. 1906, **142**, 633.
8. Ber. 1906, **39**, 1366. J. Lipski, Zts. Elektrochem. 1909, **15**, 189.
9. Zts. ang. Chem. 1909, **22**, 1234.
10. Mon. Sci. 1911, **75**, 561; Chem. Ztg. Rep. 1911, **35**, 621.
11. Chem. Ztg. 1910, **34**, 345; abst. C. A. 1910, **4**, 1653. C. Steinmetz, U. S. P. 865618, 894547, 1062805; abst. J. S. C. I. 1907, **26**, 1097; 1908, **27**, 905; 1913, **32**, 699; Mon. Sci. 1908, **69**, 56; 1909, **71**, 114; 1914, **81**, 15; C. A. 1913, **7**, 2355.
12. Wiener Landw. Ztg. **61**, 856; abst. C. A. 1912, **6**, 140.
13. J. Ind. Eng. Chem. 1918, **10**, 457; abst. C. A. 1918, **12**, 1497.
14. L'Industrie. Chim. 1918, **5**, 80; abst. C. A. 1918, **12**, 1498.
15. Engineering, 1917, **104**, 133; Chem. Trade J. 1917, **61**, 72; C. A. 1917, **11**, 2178; J. S. C. I. 1917, **36**, 777.
16. Chem. Ind. 1914, **37**, 513; abst. C. A. 1915, **9**, 356.
17. Engineering, **93**, 599; abst. C. A. 1912, **5**, 2499. See also Electro-technica, 1917, **4**, 102; Rev. gen. elec. I, 145; C. A. 1917, **11**, 2071. Engineering, 1916, 102. D. Lance and V. Elworthy, Belg. P. 190143, 1906. E. Donath and A. Indra, C. A. 1913, **7**, 2456. H. Deville, Compt. rend. 1865, **60**, 317. A. de Hemptinne, Bull. Acad. Roy. Belg. 1902, **28**. See also: Weinmann, Ber. 1875, **8**, 977. L. Mond, Zts. ang. Chem. 1898, **11**, 263. M. Lyle, Bull. Soc. Chim. 1876, **25**, 427. G. Mulder, Jahr. Chem. 1850, **3**, 290. T. Fleitmann, Ann. 1850, **76**, 127. L. Wright, J. C. S. 1881, **39**, 357; Ber. 1881, **14**, 2415. G. Johnson, J. C. S. 1881, **39**, 128; Chem. News, 1881, **43**, 42, 488. K. Williams and W. Ramsay, J. C. S. 1886, **49**, 223. O. Loew, Ber. 1890, **23**, 1443. H. Baker, Chem. News, 1883, **48**, 187. F. Varrentrapp and H. Will, Ann. 1841, **39**, 266. H. Will, Ann. 1843, **45**, 95. H. Davy, Phil. Trans. 1807, **97**, I. Rayleigh, J. C. S. 1897, **71**, 181. E. Baur, Ber. 1901, **34**, 2385. E. Permann, Chem. News, 1904, **90**, 13, 182; Proc. Roy. Soc. (A), **76**, 167. F. Haber and G. van Oordt, Zts. anorg. Chem. **43**, 111; **44**, 341; **47**, 42. H. Wolterreck, D. R. P. 146712; abst. Chem. Centr. 1903, **74**, II, 1264; F. P. 328415, 332591; abst. Compt. rend. 1909, **146**, 124. R. Nithak, D. R. P. 95532. J. Wood, U. S. P. 826301. P. de Lambilly, D. R. P. 74274, 78573. J. Schlutius, E. P. 2200, 1903. P. Kestner, Belg. P. 206108, 206109, 1908. L. Brunel and P. Woog, Compt. rend. 1908, **145**, 922; Chem. Centr. 1908, **79**, I, 209. F. McDermott, J. A. C. S. 1911, **33**, 515; abst. Chem. Zentr. 1911, **82**, I, 1541. F. Haber, Chem. Ztg. 1910, **34**, 245. Badische Anilin & Soda Fabrik., D. R. P. 223408; abst. Chem. Centr. 1910,

consulted as indicating new possible methods of application.

Recovery of Nitric Acid from Various Sources. In the original method of L. Stille,¹ the nitrous gases generated in a battery of the Bunsen or Groves type in which potassium chloride or nitrate is used in the porous shell containing the zinc element, are passed in contact with water whereby nitric acid is regenerated. When the battery is exhausted the liquid contents are mixed, and zinc carbonate is precipitated by potassium carbonate and separated, potassium nitrate being obtained from the remaining solution by evaporation and crystallization.

The manufacture of mordants by the action of nitric acid

81, II, 347. F. Haber, D. R. P. 229126; abst. Chem. Zentr. 1911, **82**, I, 49. D. R. P. 238450; abst. Chem. Zentr. 1911, **82**, II, 1184. Badische Anilin & Soda Fabrik, E. P. 19249, 1910. F. P. 425009; D. R. P. 246377; abst. Chem. Ztg. Rep. 1912, **36**, 291. Zts. ang. Chem. 1911, **24**, 352. Soc. Gen. des. Nitrures, D. R. P. 250085; abst. Chem. Ztg. Rep. 1912, 505. Gewerkschaft des Steinkohlenbergwerke Lothringen, Belg. P. 226216, 1910. Centralstelle für Wissenschaftlich-Technische Untersuchungen, E. P. 2392, 1915; abst. J. S. C. I. 1916, **35**, 360. D. R. P. 288496; abst. J. S. C. I. 1916, **35**, 360. D. R. P. 290877; abst. C. A. 1911, **5**, 874. J. Gerlache, Belg. P. 244742, 247106, 1912. W. Traube, Ber. 1905, **38**, 828. W. Traube and A. Biltz, Ber. 1904, **37**, 3130; 1906, **39**, 166. W. Woltereck, D. R. P. 146712, 1912; abst. Zts. ang. Chem. 1902, **16**, 1160; Chem. Ind. 1903, 600. Ges. f. Stickstoffdünger, Belg. P. 198691, 1907. H. Woltereck, Compt. rend. 1908, **147**, 460, 1402. R. Goldschmidt, Belg. P. 187661, 1906. F. Zeisberg, Met. Chem. Engr. 1916, **15**, 299. F. Frerichs, Belg. P. 211957, 1908. H. Mehner, Belg. P. 126614, 1897; 175472, 1904; Swiss P. 13884, 1897. Q. Moore, J. Cunningham and J. Stokes, Belg. P. 251147, 1912. W. Mueller, Belg. P. 238165, 1911. P. Mason, Belg. P. 233028, 1911. A. Michiels and L. Deboucq, Belg. P. 174140, 1903. J. Machtolf and K. Bosch, Belg. P. 213704, 1909. J. Meffert, Belg. P. 129689, 1897. H. Sulzer, Belg. P. 242325, 1912. H. Simonin, Belg. P. 220442, 1909. F. Saatmann, Belg. P. 184573, 1905. Societe pour la Traitement Rationnel des Vidanges, Belg. P. 145871, 1899. L. Sternberg, Belg. P. 130136, 1897. R. Schilling and C. Kremer, Belg. P. 171535, 178269, 1903. H. Teichmann, Belg. P. 141411, 1899. H. Woltereck, Belg. P. 167807, 170057, 1903; 178802, 1904; 190682, 1906. E. P. 2461, 1902; F. P. 328415, 332591, 1903; abst. J. S. C. I. 1903, **22**, 695, 957, 1243. C. Bosch, Aust. P. 303, 304, 1911. R. Davis and H. Bryan, U. S. P. 1319663, 1919; abst. C. A. 1920, **14**, 97; J. S. C. I. 1919, **38**, 946-A. General Chemical Co., E. P. 124762, 1919; abst. J. S. C. I. 1920, **39**, 49-A. E. Maxted, E. P. 130023, 1917; 130063, 131049, 1918; abst. C. A. 1920, **14**, 23, 97, 98. Chem. Age, 1919, **1**, 514, 540, 590; abst. J. S. C. I. 1919, **38**, 944-A. See J. S. C. I. 1918, **37**, 232-T, 368-A; 1919, **38**, 219-A. E. Maxted and T. Smith, E. P. 134572, 1918; abst. J. S. C. I. 1920, **39**, 21-A. R. Parsons, H. Jenkins and C. I. Syndicate, E. P. 130069, 1918; abst. C. A. 1920, **14**, 210. See E. P. 25415, 1913; 22867, 1914; 104600; abst. C. A. 1915, **9**, 1155; 1916, **10**, 1304. L'Air Liquide Soc. Anon., E. P. 129637, 1919; abst. J. S. C. I. 1919, **38**, 932-A. C. Toniolo, U. S. P. 1318936, 1919; abst. C. A. 1920, **14**, 97; J. S. C. I. 1919, **38**, 945-A. G. Taylor and I. Knapp, U. S. P. 1315534, 1919; E. P. 134237, 1918; abst. J. S. C. I. 1919, **38**, 818, 846-A. General Chemical Co., E. P. 120546, 124762; abst. J. S. C. I. 1920, **39**, 108-A. G. Claude, Compt. rend. 1919, **169**, 1039; U. S. P. 1332460, 1920.

1. E. P. 1732, 1863.

according to the process of J. Perino,¹ iron nitrate is employed to oxidize the sulfide and so form a soluble sulfate. The zinc ore is mixed with a considerable excess of iron nitrate and charged into a retort which is slowly heated, the nitrous fumes being condensed in water for the regeneration of nitric acid. The process of W. Wolters is similar.²

In de-tinning iron scrap in acidified ferric sulfate solution, or in a solution of sodium or potassium nitrate mixed with sulfuric acid,³ the ferric sulfate solution obtained is oxidized for use again, preferably by adding it slowly to a mixture of sodium or potassium nitrate and sulfuric acid at 170° F., the nitrous vapors given off being mixed with air or otherwise to produce nitric acid.⁴

P. de Wilde⁵ has described a process for the regeneration of nitric acid in the manufacture of calcium phosphates.⁶ Where lead and carbon are used as electrodes in primary batteries with an electrolyte consisting of a dilute solution of nitric acid and sodium nitrate, the charged electrolyte containing dissolved lead is drawn off, the lead being precipitated by the addition of sulfuric or hydrochloric acid, and the resulting nitric acid re-used in the battery.⁷ The processes for the recovery of nitric acid of I. Baggs,⁸ D. Dow and J. Telfer,⁹ and R. Rogers,¹⁰ are of minor interest in this connection.

Recovery of Nitric Acid from Absorbents. Nitric and other corrosive acids are recoverable from kieselguhr, randanite, and other absorbents with which they have been mixed to facilitate transportation, by treatment in a nitric acid distillation plant, the material being spread as a thin layer on the bottom of a retort of suitable shape, the distillation being assisted by stirring the material and by suction. The inert residue may be used again

1. E. P. 10657, 1888.

2. E. P. 16609, 1889.

3. H. Hemingway, E. P. 8759, 1902; abst. J. S. C. I. 1903, **22**, 561; Chem. Ztg. 1903, **27**, 814.

4. E. P. 8133, 1900; abst. J. S. C. I. 1901, **20**, 368.

5. E. P. 14194, 1903; abst. J. S. C. I. 1903, **22**, 1085; Chem. Ztg. 1904, **28**, 1052; Mon. Sci. 1905, **63**, 52.

6. E. P. 14112, 1903; abst. J. S. C. I. 1903, **22**, 1085; Chem. Ztg. 1904, **28**, 1052; Mon. Sci. 1905, **63**, 52.

7. M. Christensen, E. P. 4832, 1907.

8. E. P. 2938, 1870.

9. E. P. 3153, 1875.

10. U. S. P. 176813, 1876.

fates of sodium, calcium or magnesium. W. Hartmann¹ saturates the acid with iron salts, which upon further concentration separate out and protect the container against the action of the acid. The W. White method for solidifying acids to increase their safety during transport² consists in mixing with the acid a salt which will crystallize with the water of the acid so as to solidify it.

Action of Nitric Acid on Aluminium. R. Seligman and P. Williams³ have discussed the action of nitric acid and nitrating mixtures upon aluminium, and find that the most important condition upon the speed of solution is temperature, the rate of solution increasing by 100% each 10° rise, over a considerable range of temperature. The life of aluminium vessels intended for storing nitric and nitrating acids may be materially augmented by attention to this factor. The most energetic solvents are mixtures containing between 20% and 40% of nitric acid (sp. gr. 1.42) by volume, while acid of 95% HNO₃ was found to be almost without dissolving effect upon aluminium. The extreme inactivity of acid of this strength is apparently the reason the Norwegian manufacturers of synthetic nitric acid have employed aluminium containers for transportation purposes. As to the action of the normal impurities in nitric acid, the presence of chlorine up to 0.05% did not appreciably increase the solvent power of the nitric acid. Similarly, 0.01% iodine gave a negative result. Conversely, the presence of 0.04% sulfuric acid raised the dissolving power by about 70%. Lower nitrogen oxides increase the rate of attack. The effect of the physical state of the aluminium is important, the metal being much more easily attacked in the amorphous than in the crystalline state. In general, the purer the metal, the more resistant it is to the action of nitric acid. Mixed nitric and sulfuric acids attack aluminium much more energetically than either acid alone.

A. Trillat⁴ has exposed plates of commercial aluminium of 99.7% purity in closed containers to the action of nitric acid of varying strengths and at various temperatures. The following

1. E. P. 2839, 1879; abst. J. A. C. S. 1880, **2**, 301.
2. U. S. P. 475586, 1892.
3. J. S. C. I. 1916, **35**, 665; abst. C. A. 1916, **10**, 2193.
4. Bull. Soc. d'Encour. 1915, 547; abst. J. S. C. I. 1915, **34**, 874.

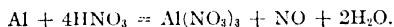
table indicates the loss of weight under the conditions stated:

| Specific Gravity of Acid | Temperature, C. | Percentage Loss of Weight | | Loss of Weight in 15 Days. Grams per Square Meter Surface |
|--------------------------|-----------------|---------------------------|-------------|---|
| | | In 15 Days | In 105 Days | |
| 1.52 | 0 | 0.54 | 1.03 | 15 |
| 1.52 | 5 | 0.92 | 1.57 | 25 |
| 1.52 | 18 | 1.42 | 2.58 | 38 |
| 1.52 | 28 | 4.27 | 6.54 | 116 |
| 1.39 | 8 | 8.76 | 16.70 | 237 |
| 1.39 | 28 | 31.10 | 58.50 | 845 |
| 1.13 | 18 | 11.78 | 22.40 | 320 |
| 1.13 | 28 | 46.10 | 82.60 | 1250 |

It has been stated¹ that aluminium is unattacked by liquids containing not less than 65% HNO_3 and not over 5% NO_2 , and this claim has been patented.

Properties of Nitric Acid. Pure, absolute nitric acid is almost impossible of preparation, and is prone to decrease in strength, owing to the liberation of oxygen and the formation of hyponitric acid, thus causing the colorless acid to turn yellow or with larger amounts of nitrogen peroxide, red. By distillation in a current of CO_2 , 98% nitric acid may readily be obtained. Fractional crystallization gives a product of maximum purity and strength of 99.4%–99.5%. Absolute nitric acid exists only in the form of a snow white crystalline mass melting at -41° . On melting a yellow liquid results which is considered to be sub-

1. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, F. P. 451812; abstr. Mon. Sci. 1912, **77**, 7. According to C. Van Deventer (Chem. Weekblad, 1907, **4**, 69; J. S. C. I. 1907, **26**, 472) aluminium is slowly attacked by nitric acid of 20%–25% strength at a temperature of 25° – 30° , for the most part according to the equation



A small quantity of free nitrogen is also produced. At atmospheric pressure a small quantity of ammonia is formed, but practically none at higher pressures. With nitric acid of a given concentration, the rapidity of the action on the metal is proportional to the surface of the metal. With acid of different concentrations, the rapidity with which the metal is attacked is proportional to the concentration of the acid. For reaction of metals and alloys with nitric acid, see J. Stansbie, J. S. C. I. 1913, **32**, 311. Also J. S. C. I. 1906, **25**, 1071; 1908, **27**, 365; 1909, **28**, 268. A. Ewart, Nature, **65**, 128; Pharm. J. 1902, **68**, 82; J. S. C. I. 1902, **21**, 368.

stantially a solution of nitric anhydride and water in nitric acid.¹

Orthonitric acid $\text{N}(\text{OH})_3$, crystallizes in needles, stable below -1.5° and melting at -35° .²

The most concentrated commercial acid has, when pure and substantially free from nitrogen peroxide, a sp. gr. of 1.50, corresponding to 94%–95% absolute HNO_3 . It begins to boil slightly above 86° , the boiling point increasing as distillation proceeds until an acid of 69% HNO_3 is reached, the temperature meanwhile rising to 126° .

The density of normal nitric acid (63.13 gm. per l.) is 1.0318 at 18.6° ,³ 1.0324 at 18° .⁴ Tables for various strengths of nitric acid are to be found in Chapter VIII of this volume. Nitric acid of high strength (sp. gr. 1.50–1.52) is a powerful oxidizing agent, and will readily inflame combustible bodies as wood and straw. W. Bousfield⁵ has studied the density and viscosity of nitric acid solutions, while H. Creighton and J. Githens⁶ have determined the boiling points and vapor tensions of nitric acids of varying concentrations and pressures. It has been found that nitrates dissolved in nitric acid increase its conductivity proportional to the amount dissolved.

The purest attainable nitric acid is stated to boil at 86°

1. F. Küster and S. Münch, *Zts. anorg. Chem.* 1905, **43**, 350; abst. J. S. C. I. 1905, **24**, 238. For freezing point curve see S. Pickering, J. C. S. 1893, **63**, 436. F. Küster and R. Kremann, *Zts. anorg. Chem.* 1901, **41**, 1.
2. H. Erdmann, *Zts. anorg. Chem.* 1902, **32**, 431; *Zts. anorg. Chem.* 1903, **16**, 1001. V. Veley and J. Manley, *Proc. Roy. Soc.* 1901, **69**, 86; abst. J. C. S. 1903, **83**, 1015.
3. R. Kohlrausch, *Wied. Ann.* 1865, **26**, 161; *Pogg. Ann.* 1865, **125**, 626; *Jahr. Chem.* 1865, **18**, 753.
4. E. Loomis, *Wied. Ann.* 1897, **60**, 532, 547; abst. *Jahr. Chem.* 1897, **50**, 98. C. Forch, *Wied. Ann.* 1895, **55**, 100; abst. *Jahr. Chem.* 1895, **48**, 94. W. Ostwald, *J. prakt. Chem.* 1877, **124**, 385. S. Arrhenius, *Zts. physik. Chem.* 1889, **4**, 96. V. Veley and J. Manley, J. C. S. 1898, **74**, ii, 290; 1901, **80**, ii, 447; 1902, **82**, ii, 135, 316.
5. J. C. S. 1915, **107**, 1405, 1781; abst. C. A. 1914, **8**, 285, 2093, 3258, 3390; 1915, **9**, 3159; J. S. C. I. 1916, **35**, 110. See also *Chem. News*, 1866, **14**, 95; 1867, **15**, 159.
6. J. Frank, *Inst.* 1915, **161**, 703; abst. *Chem. Trade J.* 1915, 165. E. Bouty, *Compt. rend.* 1888, **106**, 595, 654. T. Graham, *Phil. Trans.* 1861, 153, 373. R. Reyher, *Zts. phys. Chem.* 1888, **2**, 744; S. Pagliani and E. Oddone, *Wied. Ann. Beibl.* 1887, **11**, 415; abst. *Jahr. Chem.* 1887, **40**, 155. A. Saposhnikoff, *Zts. physik. Chem.* 1905, **53**, 225. For oxidation of dilute nitric acid in sunlight, see A. Benrath, *J. prakt. Chem.* 1911, **192**, 324; abst. J. S. C. I. 1911, **30**, 1141. For electrolysis of nitric acid, refer to F. Jeffery, J. S. C. I. 1915, **34**, 1100. The effect of temperature on the equilibrium of nitric and nitrous acids has been studied by E. Briner and E. Durand, *Compt. rend.* 1912, **155**, 582, 1495; abst. J. S. C. I. 1912, **31**, 981; 1913, **32**, 82.

with partial decomposition.¹ Nitric acid has been shown by the usual methods (rate of hydrolysis of methyl acetate, inversion of cane sugar, freezing point lowering and conductivity) to be the strongest known acid. It dissolves readily in ether, and the ether-water partition coefficients have been determined.² All its salts are soluble and there is little tendency to form complexes.

One of the chief characteristics of nitric acid is its remarkable oxidizing power, being itself capable of reduction to HNO_2 , NO_2 , NO , N_2O , $\text{H}_2\text{N}_2\text{O}_2$, NH_2OH , N_2 and NH_3 .³ Nitric acid is not affected by hydrogen at ordinary temperatures or at 100° ,⁴ but is reduced by it to ammonia by platinum sponge.⁵ Nitric acid forms nitroderivatives with many organic compounds. With cellulose and other carbohydrates, nitric acid alone causes reduction and the formation of such acids as oxalic. In the presence of sulfuric acid as a dehydrating agent, however, substitution takes place, a series of nitro groups are introduced, and inflammable and combustible but highly stable esters result. Nitric acid with alcohols yield esters, none of which at the present time are used to any considerable extent as cellulose ester solvents. Ethyl and amyl nitrates have been patented as solvents, but were

1. H. Erdmann, *Zts. anorg. Chem.* 1902, **32**, 431. J. Brühl, *Zts. Phys. Chem.* 1897, **22**, 373. V. Velej and J. Manley, *Proc. Roy. Soc.* 1901, **69**, 86.

2. S. Bogdan, *Zts. Elektrochem.* 1905, **11**, 824; 1906, **12**, 489. A. Hantzsch and F. Sebaldt, *Zts. Phys. Chem.* 1899, **30**, 285.

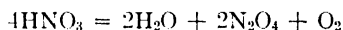
3. R. Ihle, *Zts. Phys. Chem.* 1896, **19**, 589; *abst. Jahr. Chem.* 1896, **49**, 101; *J. C. S.* 1896, **70**, ii, 460.

4. M. Berthelot, *Compt. rend.* 1898, **127**, 27.

5. R. Wagner, *Dingl. Poly.* 1867, **183**, 76. Meister, Lucius & Bruening, E. P. 10522, 1911. E. Mueller and J. Weber, *Zts. Elektrochem.* 1903, **9**, 955. W. Mueller, *Zts. Elektrochem.* 1903, **9**, 978. E. Mueller and F. Spitzer, *Zts. Elektrochem.* 1905, **11**, 509; *Ber.* 1905, **38**, 1190. J. Tafel, *Zts. anorg. Chem.* 1902, **31**, 289. R. Weber, *Pogg. Ann.* 1867, **130**, 277. For solution of metals in nitric acid, see N. Tarugi, *Gazz. chim. ital.* 1903, **33**, (ii), 171. E. Millon, *J. pharm. chim.* 1842, (iii), **2**, 179. V. Velej, *Trans. Roy. Soc.* 1891, **182-A**, 279. J. Ackworth and H. Armstrong, *J. C. S.* 1877, **32**, 54. C. Montemartini, *Atti. R. Accad. Lincei*, 1892, (5), **1**, i, 63. C. Walker, *J. C. S.* 1893, **63**, 845. P. Freer and G. Higley, *Amer. Chem. J.* 1899, **21**, 377. A. v. Bijlert, *Zts. Phys. Chem.* 1899, **31**, 131. J. Gladstone, *Phil. Mag.* 1900, (v), **50**, 231. J. Stansbie, *J. S. C. I.* 1908, **27**, 365; 1909, **28**, 274. E. Rennie, A. Higgin and W. Cooke, *J. C. S.* 1908, **93**, 1162. W. Dunstan and J. Hill, *J. C. S.* 1911, **99**, 1853. For the electrolytic reduction of nitric acid, see H. Patten, *Trans. Amer. Electrochem. Soc.* 1907, **12**, 325; *abst. J. S. C. I.* 1908, **27**, 575. For stability of nitric acid in acetic acid solution, refer to K. Orton and W. Gray, *Anal.* 1912, **37**, 303; *J. S. C. I.* 1912, **31**, 718.

soon discarded for this purpose on account of instability.

According to G. Baxter and F. Grover,¹ but refuted by J. Jannek and J. Meyer,² nitric acid when concentrated by distillation through quartz tubes contains unweighable amounts of impurities, and the acid distilled through platinum is equally pure, except minute traces of dissolved base metals.³ The decomposition of nitric acid by light has, of course, been familiar for some time, but apparently was not closely examined until 1898,⁴ when M. Berthelot showed that the products of decomposition of this acid under the influence of light are O, NO₂ and water, and that these same products are obtained when the anhydrous acid is heated in vacuum tubes at 100° for some hours in the dark. The action, which is not reversible, may be represented as follows:



V. Veley and J. Manley⁵ have observed that light appears to act only on the vapor of the acid, and not on the liquid. W. Reynolds and W. Taylor,⁶ in attempts to prepare especially pure

1. J. A. C. S. 1914, **36**, 1089; Chem. Ztg. Rep. 1915, **39**, 229.
2. Zts. anorg. Chem. 1913, **83**, 71; Ber. 1913, **46**, 2876; C. A. 1914, **8**, 846; Chem. Zentr. 1913, **84**, II, 1022; J. S. C. I. 1913, **32**, 825.
3. H. Creighton and H. Smith, J. Frank. Inst. 1915, **180**, 703; abst. J. S. C. I. 1915, **34**, 277; 1916, **35**, 110. W. Reynolds and H. Taylor, Chem. News, 1911, **104**, 315. K. Schaefer, Zts. anorg. Chem. 1916, 285; abst. C. A. 1916, **10**, 848; 1917, **11**, 425. K. Schaefer and S. Deichsel, Zts. anorg. Chem. 1916, **98**, 70; J. C. S. 1917, **112**, ii, 186; J. S. C. I. 1917, **11**, 641. J. Withrow, J. Ind. Eng. Chem. 1917, **9**, 771; abst. J. S. C. I. 1917, **36**, 1005; C. A. 1917, **11**, 2718. Chem. News, 1887, **55**, 188; 1887, **56**, 140; 1888, **58**, 263; 1889, **59**, 92; 1889, **60**, 13; 1890, **61**, 216; 1891, **63**, 210, 295; 1892, **65**, 51; 1901, **64**, 225; 1895, **71**, 293, 395. H. Creighton and J. Githens have plotted out isobaric curves showing the change in the boiling point with variation in the composition; they are approximately parallel, and their shape is that characteristic of mixtures exhibiting a maximum boiling point. The boiling point of the pure acid was found to be 82.5° at 675 mm., and the highest boiling point was obtained with a mixture containing 69.24% HNO₃ (121.8° at 760 mm.). Determinations were also made of the boiling point and composition of the mixture of maximum boiling point at 760, 360 and 110 mm. pressure, 500 cc. of mixture with 60% to 80% of nitric acid being distilled until only 15 to 20 cc. remained, and the acid content of the residue determined with standard barium hydroxide. The results confirmed the evidence given by the earlier experiments that the composition of the mixtures of maximum boiling point changes but slightly with the pressure. The mean results obtained, in good agreement with those recorded by H. Roscoe (J. Chem. Soc. 1861, **13**, 146), were: at 760 mm., 66.18% HNO₃, b. pt. 121.70°; at 360 mm., 67.15% HNO₃, b. pt. 99.9°; at 110 mm., 66.80% HNO₃, b. pt. 74.2°.
4. Compt. rend. 1898, **127**, 143.
5. Phil. Trans. 1898, **191**, 365.
6. J. C. S. 1912, **101**, 131; abst. J. S. C. I., 1912, **31**, 26.

nitric acid, came to the conclusion that appreciable decomposition of the distillate takes place through the action of diffused daylight.

Storage and Transportation of Nitric Acid. Concentrated nitric acid may be stored and transported in cast iron, wrought iron or even in lead vessels under certain conditions as to the concentration of the acid and its freedom from impurities, but dilution of the acid as by exposure to moisture often causes violent action.

H. Baggeley¹ has proposed a compound of fireclay and Cornwall or China stone to which a little asbestos or aluminium silicate may be added, as a composition for acid tanks. Crushed slate or other schistose material;² a concrete composed of finely divided magnesia and silica mixed with mineral wax and sulfur;³ artificial stone composed of serpentine, soapstone, feldspar, mica, quartz and fireclay intimately mixed, ground and baked;⁴ or artificial sandstone preferably glazed⁵ have also been advocated as materials for container for the corrosive inorganic acids.

Aluminium, either alone,⁶ or copper-aluminium,⁷ or aluminium-bronze alloys,⁸ have been extensively employed for acid resisting containers, C. Kellner⁹ having patented for this purpose an acid-proof aluminium-silicate composition formed by mixing ground slate with water-glass and Portland cement. Various alloys have been put forward from time to time as especially advantageous for this purpose, R. Grimshaw¹⁰ recommending a

1. E. P. 405, 1876.
2. R. Crompton and B. Jenkinson, E. P. 17623, 1889.
3. W. Woods, E. P. 25013, 1895.
4. B. Hess, E. P. 2321, 1883. E. de Haen, D. R. P. 197074, 1906; abst. J. S. C. I. 1908, **27**, 795; Chem. Zentr. 1908, **79**, I, 1588; Chem. Ztg. Rep. 1908, **32**, 286; Jahr. Chem. 1905-1908, I, 1988; Zts. Schiess. Spreng. 1908, **3**, 214.
5. E. Erichsen, E. P. 138, 1874.
6. Norsk. Hydro-Elektrisk Kvælstofaktieselskab, Norw. P. 22894, 1911; abst. C. A. 1913, **7**, 2289.
7. Z. d'Amico, D. R. P. 248857, 273202; abst. C. A. 1913, **7**, 279; 1914, **8**, 2869; Chem. Zentr. 1912, **83**, II, 402; 1914, **85**, I, 1796; Chem. Ztg. Rep. 1912, **36**, 475; 1914, **38**, 316; Wag. Jahr. 1912, **58**, I, 364; 1914, **60**, I, 285; Zts. ang. Chem. 1912, **25**, 1705; 1914, **27**, 357.
8. J. Whitley, E. P. 10022, 1886.
9. C. Kellner, E. P. 6952, 1890. For formulas for acid resisting cements, see A. Holley and H. Webb, U. S. P. 1287995, 1288413; abst. C. A. 1919, **13**, 504.
10. Chem. Eng. **17**, No. 2; Chem. News, 1913, 283. Metal Ind. **10**, 498; abst. C. A. 1913, **7**, 584.

cobalt-copper-tin combination, while plated zinc-alloy,¹ lead alloy,² lead-coated with gutta percha,³ chromium-iron,⁴ carrying 2%–5% molybdenum, lead with 2% antimony,⁵ lead-copper-antimony,⁶ lead-antimony-graphite,⁷ or metals of the nickel group with small amounts of the platinum series of metals,⁸ have also been patented for this purpose.

Iron rendered passive in various ways, or silica, or the two combined have given excellent results for both weak and concentrated acids. Iron electrolytically coated with a noble metal,⁹ or previously heated to incandescence to deposit on the surface an acid-resisting coating of oxide,¹⁰ or iron vessels lined with sulfur,¹¹ or gutta percha¹² have been proposed. Corrosiron,¹³ duriron, tant-iron or "neutral iron"¹⁴ are high silicon-iron alloys containing from 8%–15% silicon. Their greatest drawback is brittleness.¹⁵ Car-

1. J. Weems, E. P. 2944, 1861.
2. I. and J. McDougall, R. Hartley and T. Sugden, E. P. 7061, 1888.
3. T. Bell, E. P. 2350, 1880. The I. Wolf apparatus for storing and transporting corrosive chemicals, U. S. P. 1285537; abst. C. A. 1919, **13**, 202.
4. W. Borchers and P. Monnartz, D. R. P. 246035; abst. C. A. 1912, **6**, 2392; Chem. Zentr. 1912, **83**, I, 1599; Chem. Ztg. Rep. 1912, **36**, 310; Wag. Jahr. 1912, **58**, I, 277; Zts. ang. Chem. 1912, **25**, 1214.
5. E. Hoyt, Brass World, June 1913.
6. H. Egells, E. P. 5894, 1883.
7. R. Meyer, E. P. 1483, 1880.
8. W. and R. Borchers, D. R. P. 265076, 265328, 278902, 278908; abst. Chem. Zentr. 1913, **84**, II, 1444, 1534; 1914, **85**, II, 1083; Chem. Ztg. Rep. 1913, **37**, 596; 1914, **38**, 524; Wag. Jahr. 1913, **59**, I, 350; 1914, **60**, I, 275; Zts. ang. Chem. 1913, **26**, 690; 1914, **27**, 635.
9. F. Busch, E. P. 180, 1863.
10. Soc. Anon. de Produits Chim. de Droogenbosch, E. P. 25094, 1899.
11. E. Parnell, E. P. 445, 1870.
12. J. Shedlock, E. P. 5498, 1880.
13. Chem. Trade J. **59**, 7.
14. W. Strzoda, E. P. 26732, 1913; abst. J. S. C. I. 1914, **33**, 643. D. R. P. 272158; abst. C. A. 1914, **8**, 2608; Chem. Zentr. 1914, **85**, I, 1392; Chem. Ztg. Rep. 1914, **38**, 269.
15. J. Brown, Science, 1916, **43**, 758; abst. C. A. 1917, **11**, 2061. Studies of the properties of iron in nitric acid of various dilutions were made with a view to throwing light on the subject of passivity. The electromotive force of the cell, iron-, nitric acid solution-, concentrated nitric acid-platinum was measured at room temperature, using nitric acid solutions of densities varying from 1.01 to 1.41 with the iron both at rest and in motion. With the iron kept at rest in acids up to 1.17 the presence of ferric nitrate increases the electromotive force in acids denser than 1.17, the electromotive force is lowered by a substance, possibly a basic ferric nitrate compound, which forms a red liquid film over the oxidized surface of the iron. In acids denser than 1.5 an explosive action takes place between the ferric oxide and the red liquid, after which the iron assumes the passive state and the electromotive force after falling to a minimum, rises slowly to a constant. The presence of a protective film on the passive iron cannot be detected, but the rise

bon silicide,¹ artificial stone high in silica;² wood covered with silicate of potash;³ ground glass or flint admixed with bitumen;⁴ or silicate of soda;⁵ pure silica in the fused state;⁶ or pig-iron rich in silicon,⁷ up to 15%,⁸ or iron properly protected with gutta percha have given excellent results in practice. O. Kowalke⁹ has recorded the acid-resisting properties of iron-silicon alloys. N. Swindin¹⁰ has detailed drawings and suggestions for the design of pipes, pans, vessels and stills for nitric and sulfuric acid concentration using ferro-silicon alloys. H. Cuau¹¹ enamels sheet iron, while M. Audouin¹² alloys chromium oxide with iron oxide as in chrome iron ore for the preparation of acid-repellant vessels.

For the concentration, especially of sulfuric acid and its

in the potential seems to indicate the expulsion of a gas from the metal. For properties of "tantiron," see Engineering, 1918, **106**, 154; Chem. Zentr. 1919, **90**, 11, 255. W. Carnell, J. Ind. Eng. Chem. 1916, **8**, 922. Chem. Zentr. 1918, **89**, 1, 887. "Monel" metal, J. Arnot, Engineering, 1918, **106**, 451; Chem. Zentr. 1919, **90**, 1, 273.

1. Siemens & Co., E. P. 21347, 1905; abst. J. S. C. I. 1906, **25**, 122.

2. F. Jurschina and R. von Gumesch, E. P. 16468, 1890.

3. Soc. Anon. de Enduits Archambault, E. P. 21148, 1900; abst. J. S. C. I. 1901, **20**, 252.

4. J. Stringfellow, E. P. 23981, 1898. The S. Viesi system of elevating and transporting corrosive and explosive liquids is detailed in Belg. P. 255831, 1913.

5. R. Panzl and A. Toretcher, E. P. 3975, 1900; abst. J. S. C. I. 1901, **20**, 27; Chem. Ztg. 1901, **25**, 570.

6. L. Schlossberg, E. P. 6949, 1913; abst. C. A. 1914, **8**, 2932; J. S. C. I. 1913, **32**, 979.

7. H. Uelsmann, E. P. 22, 1880.

8. H. Uelsmann, E. P. 3456, 1880. British Dyes, Ltd., J. Turner and J. West (E. P. 124997; abst. J. S. C. I. 1919, **38**, 313-A) have described a tank for transporting liquids by rail.

9. O. Kowalke, Amer. Electrochem. Soc. May 1917, abst. J. S. C. I. 1917, **36**, 1097. A number of iron silicon alloys, containing 1.2% to 19.8% silicon, were immersed in 10% solutions of sulfuric, hydrochloric, nitric, acetic and citric acids for periods ranging from 51 hours to 29 days at 20° to 35° C., and the losses determined. With few irregularities the resistance to acid attack was a minimum at 1.2% to 3.3% silicon and a maximum at 16%-18% silicon. The alloys were made from electrolytic iron and ferro-silicon melted together in graphite crucibles lined with magnesium oxide and cast in a graphite mould. The alloys of low silicon content made good soft castings, but above 3.5% silicon the alloys were brittle; the test pieces of the brittle alloys were ground to obtain fairly smooth surface. The alloys containing 3% to 5% silicon were not excessively brittle, but were very readily attacked by sulfuric, hydrochloric, acetic and citric acids. The alloys containing 16%-18% silicon were exceedingly resistant to mineral acids, but were so brittle that they could not be machined.

10. Chem. Trade J. 1916, **59**, 323; Met. Chem. Eng. 1916, **15**, 647; abst. C. A. 1917, **11**, 1.

11. E. P. 2392, 1878.

12. E. P. 1398, 1876.

storage, wood vessels lined with lead,¹ or coated with mixtures of asbestos² with shellac,³ or paraffin,³ or celluloid,⁴ or a mixture of asbestos, clay, liquid silicate and glycerol.⁵ Nitrocellulose,⁶ and celluloid;⁷ silicates and celluloid,⁸ or molten sulfur have also been proposed, but not extensively used for this⁹ purpose. Rubber,¹⁰ especially after vulcanization;¹¹ india rubber paints;¹² india rubber, asbestos and sulfur;¹³ and other rubber-containing compounds,¹⁴ have especially more recently been highly recommended for their durability and value with acids of varying degrees of strength. Ebonite¹⁵ or paraffin,¹⁶ sulfur and graphite;¹⁷ Trinidad asphalt,¹⁸ or bitumen and paraffin;¹⁹ rosin and turpentine;²⁰ "stearic pitch paint;"²¹ sulfur and linseed oil;²² litharge and linseed oil;²³ either with or without pitch²⁴ have received patent protection as especially meritorious combinations for this purpose.

Glass,²⁵ which may be coated with paraffin²⁶ as acid containers, has a limitation as to size. R. Jordan coated the glass with

1. R. Weare, E. P. 252, 1875. See "Acid-proof Alloys," C. Rossi, E. P. 121730, 1918; abst. C. A. 1919, **13**, 836.
2. R. Rhodes and G. Binswanger, E. P. 2501, 1882.
3. E. Borsari, E. P. 14919, 1899.
4. D. Hawes, E. P. 1228, 1896.
5. G. Meyer, E. P. 941, 1883.
6. A. Oblasser and C. Theryc, E. P. 19242, 1892.
7. P. Funfak, E. P. 25031, 1896.
8. E. Fahrig, E. P. 1897, 1890.
9. T. Owen, E. P. 21294, 1892.
10. G. Thomson and G. Watson, E. P. 2913, 1874.
11. W. Hayhurst, E. P. 109194, 1917; abst. J. S. C. I. 1917, **36**, 1121; C. A. 1918, **12**, 3.
12. Ernst. Chem. Apparatur, 1916, 93; Zts. ang. Chem. 1916, **28**, ii, 370.
13. T. Mercier, E. P. 3748, 1893.
14. M. Dittenhoefer, E. P. 2992, 1888. J. Knight, E. P. 852, 1861.
15. H. Traun, E. P. 26577, 1908; abst. J. S. C. I. 1910, **29**, 141.
16. F. and F. Welleba and F. Uffenheimer, E. P. 7208, 1890.
17. J. Holden, S. Turton and J. Barber, E. P. 2288, 1877.
18. S. Tanari, E. P. 107370, 1917; abst. J. S. C. I. 1918, **37**, 188-A; Jap. P. 29986, 1916; abst. C. A. 1917, **11**, 543.
19. Min. and Eng. World, Mar. 28, 1914; abst. J. S. C. I. 1914, **33**, 420. See also Chem. News, 1868, **17**, 266, 290; 1871, **24**, 47, 74.
20. J. Field, E. P. 21650, 1902; abst. J. S. C. I. 1903, **22**, 1188.
21. F. Bonstein, U. S. P. 1207845; abst. C. A. 1917, **11**, 543.
22. C. Morfit, E. P. 2545, 1872.
23. F. Iefelmann, E. P. 1828, 1900; abst. J. S. C. I. 1901, **20**, 233.
24. C. Grist, E. P. 21742, 1895.
25. E. Teisler, E. P. 7597, 1900.
26. J. Holden, E. P. 3834, 1876. For properties of monel metal, consult J. Arnott, Engineering, 1918, **106**, 451; abst. C. A. 1919, **13**, 220.

asphalt-cement;¹ C. Meigs² mixes finely divided silica, apatite and sodium silicate; or by first treating the silica with a chloride, nitrate or sulfate,³ while I. Schlossberg⁴ combines silicic anhydride with soluble glass, saturates with fluosilicic acid, then roasts. Wood oil⁵ has been patented as a material for rendering wooden vessels chemical proof. To render valves acid-proof, G. Kessler⁶ covers the exposed surfaces with mica flakes cemented together by means of an acid resisting binder. Asphalt, calcium sulfate and fine silica makes an excellent composition for lining acid containers.⁷

The acid vessels of the Parazone Co.,⁸ Hart Accumulator Co.,⁹ J. Paterson and A. Oke,¹⁰ J. Larkin,¹¹ J. Field,¹² and the Berliner Apparatebau Ges.¹³ offer little that is new. H. Morris¹⁴ has proposed subaqueous tanks for the transportation of nitric acid. The Aktienges. fuer Anilin-fabrikation¹⁵ describe an aspirator connected siphon for emptying acid carboys, while the Badische Anilin- und Soda-fabrik¹⁶ have devised an apparatus for running off acids consisting of a disc protecting the workmen from any acid squirting out and against the inhalation of acid fumes. The W. Pilkington glass acid duct,¹⁷ the detachable hood for acid vessels of W. Lynes,¹⁸ the E. Keller acid collecting apparatus,¹⁹ the

1. D. R. P. 280863; abst. Chem. Zentr. 1915, **86**, I, 184; Chem. Ztg. Rep. 1915, **39**, 6; Zts. ang. Chem. 1915, **28**, 118.
2. U. S. P. 1237078, 1917; abst. C. A. 1917, **11**, 2948; J. S. C. I. 1917, **35**, 1010.
3. C. Meigs, U. S. P. 1252013; abst. C. A. 1918, **12**, 757; J. S. C. I. 1918, **37**, 125-A.
4. E. P. 9394, 1909; abst. J. S. C. I. 1909, **28**, 1200.
5. A. Kronstein, E. P. 2679, 1901; abst. J. S. C. I. 1901, **20**, 460.
6. G. Kessler, D. R. P. 289599, 1913; abst. C. A. 1916, **10**, 2544; Chem. Zentr. 1916, **87**, I, 319; Chem. Ztg. Rep. 1916, **40**, 73.
7. U. S. P. 1185722, 1916; abst. C. A. 1916, **11**, 2028.
8. Parazone Co. and H. Gardiner, E. P. 18201, 1891.
9. E. Clark and Hart Accumulator Co., E. P. 15512, 1904.
10. E. P. 3491, 1897.
11. J. Larkin, E. P. 7323, 1892.
12. E. P. 21650, 1902; abst. J. S. C. I. 1903, **22**, 1188.
13. E. P. 13989, 1905.
14. J. S. C. I. 1916, **35**, 1243. H. Morris and N. Turnbull, E. P. 106351; abst. J. S. C. I. 1917, **36**, 698.
15. D. R. P. 258341; abst. C. A. 1913, **7**, 2711; Chem. Zentr. 1913, **84**, I, 1478; Chem. Ztg. Rep. 1913, **37**, 244; Wag. Jahr. 1913, **59**, I, 665; Zts. ang. Chem. 1913, **26**, 281.
16. Zts. f. Gewerbehyg. 1912, 85; Chem. Ztg. Rep. 1912, **36**, 416.
17. E. P. 2111, 1874.
18. E. P. 14615, 1902; abst. J. S. C. I. 1903, **22**, 484.
19. U. S. P. 1247280, 1917; abst. J. S. C. I. 1918, **37**, 56-A.

P. Channon syphon for corrosive liquids,¹ and the acid containing vessels of A. Bontempi,² G. Liddiard,³ and J. Marx,⁴ are best understood from reference to the original drawings and patent descriptions. R. Roth⁵ has described a brush for applying corrosive liquids in which the bristles are glass and fused to a glass tube. Drawings, description and explanation of the action of various acid eggs, elevators and gas compressors for both intermittent and continuous discharge for the handling of acids are to be found in *Met. Chem. Eng.* **8**, 375.

In contradistinction to the difficulties encountered in the storage and transportation of nitric acid, mixed nitrating acid, sulfuric acid and oleum on the contrary, have a diminished corrosive action on wrought iron. For their transportation, therefore, special composition railway tank cars consisting of large boiler-like vessels are used, of capacity up to 50 tons of acid per tank car. Storage may be effected in similar vessels, being transferred from the tank cars by means of compressed air ("blown over"). With the more concentrated sulfuric acids and oleums, these cars have steam pipes contained therein, so that the solid mass in cold weather may be liquefied by heat and this condition transferred by compressed air from one container to another. Where possible, acid storage capacity is usually placed on such elevations that, with respect to the nitrating houses, gravity flow may be taken advantage of. Where mixtures high in SO_3 are operated upon, highly irritating white fumes are evolved and escape as soon as the compressed air is turned off. This inconvenience may be partially obviated by interposing a container of concentrated sulfuric acid, which acts as an absorbent.⁶

Fuming Nitric Acid is a red fuming liquid, possessing pow-

1. E. P. 112188, 1917; abst. J. S. C. I. 1918, **37**, 81-A.
2. E. P. 18742, 1906; abst. J. S. C. I. 1907, **26**, 325.
3. E. P. 14092, 1905; abst. J. S. C. I. 1906, **25**, 167.
4. E. P. 22640, 1897.
5. E. P. 24558, 1911.
6. Anon., *Met. Chem. Eng.* 1910, **8**, 375; abst. C. A. 1910, **4**, 2030. See also: M. Prentice, E. P. 4392, 1875. G. Adamson, U. S. P. 846541. Vorster and Grunberg, D. R. P. 24748; abst. *Mon. Sci.* 1884, **26**, 510; *Wag. Jahr.* 1883, **29**, 356. F. Hale and A. Scott, E. P. 24379, 25386, 1910; abst. C. A. 1912, **6**, 1504, 1505; J. S. C. I. 1911, **30**, 1251; *Chem. Ztg. Rep.* 1912, **35**, 170, 194. C. Schärtler, *Zts. ang. Chem.* 1901, **14**, 729. The H. Tobler acid pump is described in U. S. P. 1282145, 1918; *Can. P.* 198770, 1920; abst. J. S. C. I. 1919, **38**, 34-A. The pump comprizes two cylinders having similarly arranged inlets and outlets, each are provided with an internal flexible

erful oxidizing properties, and produced by adding $\text{HN}\ddot{\text{O}}_2$, N_2O_3 or NO to nitric acid; by distilling niter with acid potassium sulfate; or by adding kieselguhr previously saturated with formaldehyde, to concentrated nitric acid.¹ As prepared by any of the above methods it contains varying amounts of NO_2 ,² and in the case where NO is used in its preparation, may be supposed to be formed either by the direct union with oxygen, or as represented by the equation



the latter then giving NO_2 with the excess of nitric acid. The intermediate production of nitrous acid is shown by the addition of water to the combination, which turns green, blue, and finally becomes colorless.³

Specific gravity tables for fuming nitric acid have been prepared by G. Lunge and L. Marchlewski,⁴ and are given in Chapter VIII of this volume. Fuming nitric acid powerfully oxidizes organic compounds to CO_2 and water, any sulfur or phosphorus present being oxidized to sulfuric and phosphoric acids respectively.⁵ Fuming nitric acid is never used as a constituent tube connecting the inlet and outlet. The inlets are connected with a pipe supplying the liquid to be pumped and the outlets with a discharge pipe. The cylinders are connected respectively with the opposite ends of a third cylinder provided with a reciprocating piston which alternately forces water or other suitable liquid into and withdraws it from the cylinders containing the flexible tubes. The flexible tubes are consequently alternately contracted and expanded, and the acid liquid is discharged through the outlet connected with the contracted tube and a fresh quantity drawn in through the inlet connected with the expanded tube. The construction of the A. Mauser metallic transport vessel for acid is described in D. R. P. 265274, 1911; abst. C. A. 1914, **8**, 1891; Chem. Ztg. Rep. 1914, **38**, 62. For apparatus for pumping corrosive liquids, see A. Human, G. Cross, U. S. P. 1323864, 1919; E. P. 115254, 1917; abst. J. S. C. I. 1918, **37**, 358-A; 1920, **39**, 54-A.

1. L. Vanino, Ber. 1899, **32**, 1392. Compare E. Mitscherlich, Pogg. Ann. 1830, **18**, 157. C. Brunner, J. prakt. Chem. 1854, **63**, 384; Jahr. Chem. 1854, **7**, 313; Dingl. Poly. 1861, **159**, 355; Jahr. Chem. 1861, **14**, 154; E. Schaller, Chem. Ztg. 1904, **28**, 594. D. Gernez, Jahr. Chem. 1872, **25**, 137. R. Haas, Ber. 1881, **14**, 597. G. Lechartier, Compt. rend. 1886, **102**, 539. L. Archbutt, J. S. C. I. 1896, **15**, 84; Jahr. Chem. 1897, **50**, 568.

2. L. Marchlewski, Zts. anorg. Chem. 1892, **1**, 363; Ber. 1891, **24**, 3274; Jahr. Chem. 1892, **45**, 597.

3. L. Marchlewski and B. Liljenstein, Zts. anorg. Chem. 1892, **2**, 18; 1894, **5**, 288.

4. Zts. anorg. Chem. 1892, **1**, 363. Refer to C. Montemartini, Atti Accad. dei Lincei, 1892, A, 63. A. Hoffmann, Ber. 1870, **3**, 658; K. Kraut, Ber. 1881, **14**, 301; Arch. Pharm. (3), **24**, 801.

5. L. Garius, Ber. 1870, **3**, 697. See Chem. News, 1900, **81**, 110. K. Lund, Dingl. Poly. 1873, **207**, 512; Jahr. Chem. 1873, **26**, 1015. S. Feldhaus, Zts. anal. Chem. 1862, **1**, 426. Verein Chemischer Fabrik in Mannheim, Belg. P. 259983, 1913; Swiss P. 65917, 68830.

of nitrating baths for the formation of nitrocelluloses or in the nitration of carbohydrates.

Detection of Nitrous Acid. The following four tests are reliable:

1. *Acetic Acid Test.* Acetic acid added to a nitrite in a test tube inclined as indicated under the ferrous sulfate test for nitric acid produces a brown ring, which nitrates do not give. If potassium iodide is present iodine is liberated. The free iodine may be absorbed by chloroform, carbon tetrachloride, tetrachlorethane or carbon bisulfide, and colors the reagents pink. Starch solution is colored blue.

2. *Potassium Permanganate Test.* Sulfuric acid solutions of potassium permanganate are decolorized by nitrous acid or a nitrite. This test detects nitrous in nitric acid, in the absence of other reducing substances.

3. *Dimethylaniline Test.*¹ 8 gm. dimethylaniline and 4 gm. HCl are made up to 100 cc. with water, of which reagent 3 drops together with 1 drop HCl is added to 50 cc. of the solution to be examined. In 15–30 minutes a yellow color due to the formation of β -nitrosodimethylaniline is developed. This is matched in a colorimeter or tintometer with the color developed by the use of a known amount of a sodium nitrite solution containing 1 part per 100,000. The presence of nitrates is said not to interfere, and the reaction sufficiently delicate to detect one part HNO_2 per million.

4. According to A. Leclerc,² nitrous acid is liberated from its salts by the addition of a syrupy solution of citric acid, and detected by the formation of the brown ring at the surface of contact of a superimposed ferrous sulfate solution. Nitrates not being decomposed by citric acid do not respond to this test.

Detection of Nitric Acid. The following qualitative tests for the presence of nitric acid are reliable in the absence of the

1. E. Miller, *Anal.* 1912, **37**, 345. W. Fischer and N. Steinbach, *Zts. anorg. Chem.* 1912, **78**, 134; *J. C. S.* 1912, **102**, ii, 1093; *J. S. C. I.* 1912, **31**, 1029.

2. *J. pharm. chim.* 1913, **8**, 299; abst. *J. S. C. I.* 1913, **32**, 975. For the determination of nitrites by means of thiocarbamide (thiourea), see M. Coade and E. Werner, *J. C. S.* 1913, **103**, 1221; abst. *J. S. C. I.* 1913, **32**, 769. For the use of sodium paratungstate in the determination of nitrogen pentoxide, see F. Gooch and S. Kuzirian, *Amer. J. Sci.* 1911, **31**, 497; abst. *J. S. C. I.* 1911, **30**, 800.

impurities and other bodies as previously has been stated.¹

1. *Ferrous Sulfate Test.* From 1 to 2 cc. of the material to be tested is added to 15-20 cc. concentrated sulfuric acid in a test tube. After the mixture has cooled the test tube is inclined and an equal volume of saturated ferrous sulfate solution is allowed to carefully flow down the inclined test tube onto the surface of the material to be tested. The tube is now righted and gently tapped. In the presence of nitric acid a brown ring forms at the juncture of the two liquids. The ferrous sulfate should be present in large excess or the brown color may be destroyed by the free nitric acid. Traces of nitric acid in sulfuric acid produce a pink color with the sulfuric acid solution of the ferrous sulfate.

Bromides, bromates, iodides, iodates, chlorates, chromates, permanganates and ferro- and ferri-cyanides interfere.

2. *Diphenylamine Test.*¹ Diphenylamine dissolved in concentrated sulfuric acid is added to 2-3 cc. of the substance to be tested in a watch glass. Upon carefully warming a blue color is produced in the presence of nitrates. Nitric acid in sulfuric acid is detected by placing a minute crystal of diphenylamine in 3-4 cc. of the acid and warming gently.

Chlorine, chlorates, bromates, iodates, chromates, permanganates, selenates and ferric iron interfere.

3. *Copper Test.* A strip of copper placed in a solution containing nitric acid evolves brown fumes.

4. *Alkaloidal Test.* Perhaps the most characteristic test for nitric acid is that developed with brucine and concentrated sulfuric acid, which gives a red color. Arbutine and berberine under similar conditions give a deep yellow and dark brownish red color respectively.²

Cinchonamine nitrate is nearly insoluble in water.³

5. *Phenolsulfonic Acid Test* is used primarily in water analysis.

6. *Di-9,10-monoxypheanthrylamine* dissolved in strong sulfuric acid forms a delicate test for nitric acid in the absence of other oxidizing substances. 0.01 gm. is dissolved in 100 cc. conc. H_2SO_4 and 0.1 gm. of the substance to be tested is added to 2

1. Chem. News, 1905, **91**, 190.

2. C. Reichard, Chem. Ztg. 1906, **30**, 790.

3. B. Howard and O. Chick, J. S. C. I. 1909,

cc. of the reagent, when, if nitrates be present, a blue color which first forms soon turns to a claret red. Nitrous acid does not alter the color unless it becomes oxidized to nitric acid.¹

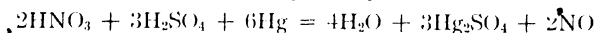
Determination of Nitrogen by Nitrometer. The principle of the nitrometer for the estimation of nitrogen acids either alone or in combination as in nitrocellulose and in mixed acids, is the reaction between the nitrogen acids, sulfuric acid and mercury, which converts all nitrogen compounds into nitric oxide, and the

1. J. Schmidt and H. Lumpp, Ber. 1910, **43**, 787, 794; abst. C. A. 1910, **4**, 1725. See also Chem. News, 1860, **1**, 131; 1862, **5**, 3; 1863, **8**, 235; 1870, **21**, 250; 1878, **38**, 58; 1884, **50**, 33; 1885, **51**, 39; **52**, 321; 1886, **54**, 37; 1889, **59**, 278; 1896, **73**, 103. A. Tingle (J. S. C. I. 1915, **34**, 393) cautiously heats in a test tube with a solution of 6.6 parts salicylic acid in H₂SO₄. A drop of the mixture is placed on a cold white porcelain slab and 2 drops KOH solution added—enough to make the drop alkaline. The development of a yellow or orange color is indicative of the presence of nitrates. H. Sen and B. Dey (Zts. anorg. Chem. 1912, **74**, 52; abst. J. S. C. I. 1912, **31**, 205), adds to a saturated solution of hydrazine sulfate (Zts. anorg. Chem. 1911, **71**, 236; abst. J. S. C. I. 1911, **30**, 1011), and is then tested for nitrate by diphenylamine. While traces of nitric acid are formed when nitrites are decomposed by urea or by boiling with ammonium chloride, this is not the case when hydrazine sulfate is used.

According to W. Iwanow (Chem. Ztg. 1912, **36**, 1170; J. C. S. 1912, **102**, ii, 1093; J. Russ. Phys. Chem. Soc. 1912, **44**, 1772; J. S. C. I. 1912, **31**, 1028; 1913, **32**, 82) the use of diphenylamine in testing sulfuric anhydride and fuming sulfuric acid for nitric acid is unreliable under ordinary conditions, since an acid containing over 20% of free anhydride gives a pink to blue coloration with this reagent. To test an acid containing, say 30% of free anhydride, it should be first diluted with about twice its volume of pure sulfuric acid of sp. gr. 1.84 so as to produce approximately the monohydrate, which gives no coloration in the absence of nitric acid. The diphenylamine test may be used in the absence of nitric acid to give a rough estimate of the percentage of anhydride in fuming sulfuric acid.

H. Caron has found (Ann. Chim. Analyt. 1911, **16**, 211; J. S. C. I. 1911, **30**, 837) that the sensitiveness of the diphenylamine test for nitrates depends mainly upon the proportion of diphenylamine and the concentration of sulfuric acid in the reagent and the rise of temperature produced on mixing the solution with the reagent. The best results are obtained with very low concentrations of diphenylamine and high concentrations of sulfuric acid, and the method of carrying out the test recommended is to add 5 cc. of a solution of 2 mgrms. of diphenylamine in 100 cc. of concentrated sulfuric acid to 2 cc. of the solution under examination. If the solution contains chlorides, it is better to use a reagent prepared by dissolving a few mgrms. of diphenylamine in a mixture of 100 cc. of sulfuric acid, 40 cc. of water and 2 or 3 cc. of 10% hydrochloric acid; 5 cc. of reagent are added to 0.5 cc. of the solution to be tested. The reaction may be masked by organic substances such as methyl and ethyl alcohols, glycerol, ether, acetone, hydrocarbons, salicylic acid (J. S. C. I. 1911, **30**, 711), and phenol, especially when the solution of diphenylamine in concentrated sulfuric acid is used, and it is therefore better to use the dilute reagent containing hydrochloric acid, mentioned above, when organic matter is present. Denigès (Bull. Soc. Pharm. Bordeaux, 1914; Ann. Chim. Analyt. 1914, **19**, 221; J. S. C. I. 1914, **33**, 221. Bull. Soc. Chim. 1911, (4), **9**, 537; J. S. C. I. 1911, **30**, 828) claims that hydro-strychnine is excellent for the colorimetric detection of nitric acid.

chemical reactions involved may be expressed as follows:



Of the three types of nitrometers described herein, the Lunge two-bulb instrument is the simplest in execution but involves corrections for temperature, pressure and vapor tension, which are automatically taken care of in the gas volumeter and the Du Pont five-part nitrometer.

An amount of nitric acid containing compound must be taken which will give a volume of NO between 100 cc. and 150 cc. The nitrometer capacity should be 150-200 cc., and contain a bulb at the top of 100 cc. capacity, the three-way stop-cock being very accurately ground.

Determinations of Nitrogen by Lunge Two-Bulb Nitrometer.

This nitrometer consists of two tubes as shown in the diagram (Fig. 83), the bulb of the decomposition tube "B" having a volume slightly under 100 cc. The graduation starts from the 100 cc. mark just below the bulb as shown and extends down the stem of the nitrometer to 140 cc. This stem is drawn out at the bottom and is graduated in 0.1 cc. The top of the tube terminates in a Friedrich-Greiner tap with two oblique passages. Above the tap is the cup "A" and a side tube attached thereto. In one position of the tap the measuring tube communicates with the side tube in the tap; in a second position it communicates with the cup "A," and in the third position the tap is closed.

The measuring tube "B" is connected by means of thick-walled rubber tubing with a pressure tube "C," the latter being a simple cylindrical glass tube of the same diameter as the measuring tube expanded with an open bulb somewhat larger than the decomposition bulb "B." It is drawn out at the bottom for the attachment of the rubber tubing, both tubes being held by clamps in which they may be moved.

To use the apparatus for the assay of mixed acid or nitric acid, the tube "C" is placed so that its lower end is somewhat

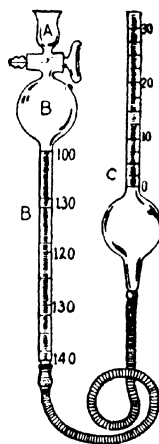


FIG. 83.—LUNGE
TWO-BULB
NITROMETER
(A, cup; B, measur-
ing tube; C, pres-
sure tube)

higher than the tap between "A" and "B" and mercury is poured in through "C," the tap "B" being open until it enters the cup "A." As the mercury enters "B" from below, no air bubbles should be formed on the side of the tube. The tap is then closed and mercury in the cup allowed to flow out through the side passage of the tap, the pressure tube lowered and the tap closed. A weighed quantity of the nitric acid or mixed acid is then introduced into the cup "A" from a pipette, the pressure tube "C" being lowered, the tap carefully opened and the acid drawn into the measuring tube by suction, care being taken, of course, not to admit any air. The cup is then rinsed with sulfuric acid free from nitrogen acids, which is similarly drawn into the measuring tube and the washing operation repeated several times. The decomposition is started by removing "B" from its clamp and thoroughly mixing the acid and mercury by repeatedly holding the tube almost horizontal, care being taken that no acid gets into the rubber tubing, and then sharply raising it to a vertical position. The tube is shaken for one or two minutes and until no more gas is evolved.

The two tubes are then adjusted so that the mercury in "C" is as much higher than that in "B" as is necessary to compensate for the layer of acid in the latter, remembering that 1 mm. of mercury has a density equivalent to about 7 mm. of acid. After the temperature has become equalized by standing for about one-half hour, the pressure is exactly adjusted by pouring a little acid into the cup "A" and cautiously opening the tap. If the gas is under diminished pressure—which is preferably the case—it will flow into "B," in which instance the tap is at once closed before air can enter, and the operation repeated after raising the pressure tube slightly. If, on the contrary, the enclosed gas tends to force its way through the acid, the tap is closed, the pressure tube lowered slightly and the tap reopened. The volume of the gas, the barometric pressure, and the temperature are then read, the latter by means of a thermometer hung in contact with the measuring tube and as near as possible to the middle of the column of gas. The barometer reading is corrected as shown in the tables in Chapter VIII of this volume. A "solubility" correction to allow for the solubility of nitric oxide in sulfuric acid is finally applied, the amount depending upon the material under examination.

When the determination is completed the measuring tube "B" is lowered so that no air enters upon opening the tap, and the gas expelled by raising the pressure tube "C," the acid being forced through a side tube of the tap and the last traces removed with filter paper. The nitrometer is then read for the gas determination. It is necessary to make sure that the tap of the nitrometer fits tightly and this is best secured by lubricating with a small amount of vaseline, care being exercised that no vaseline gets under the tap and so comes in contact with the acid, as this causes the formation of froth, which settles very slowly. While a glass tap cannot be expected to remain entirely air-tight for any considerable length of time when exposed to variations in pressure, the tap can, however, be regarded as satisfactory if no air enters the measuring tube during an interval of two hours after it has been completely filled with mercury and the pressure tube lowered.

The nitrometer may be calibrated by slowly running out re-distilled water at a temperature of 20° and weighing the volumes delivered; the true capacity in absolute centimeters being calculated from the weights obtained. It is imperative that a uniform sulfuric acid be used for nitrometer determinations and for this purpose pure sulfuric acid free from nitrogen is diluted to 94%-95% strength. The solubility of nitric oxide gas in sulfuric acid varies with the concentration of the latter, being at a minimum in 70% H_2SO_4 and increasing with weaker or stronger acid. It is inconvenient in practice, however, to employ acid weaker than about 90% on account of the increasing quantity of mercurous sulfate precipitating from the weaker acids, which tends to obscure the reading. Variation in the amount of acid used will produce corresponding variation in the volume of nitric acid observed because more gas will be dissolved in an increased bulk of acid. Therefore, there is an obvious advantage in operating with a minimum of acid, this practical minimum being about 15 cc., it having been found that the bulb and tube become coated with mercurous sulfate unless this is employed, and furthermore, a combination of mercury, mercury salt and acid tend to produce a tenacious emulsion during the shaking where a minimum amount of acid has been used. This difficulty may be partly obviated by washing the bulb and tube with fresh acid after each decom-

position but this practice in general is objectionable because the acid added after the decomposition may take up an uncertain amount of nitric oxide and is not likely to become saturated.

At the close of each day's work the mercury in the decomposing bulb of the nitrometer should be thoroughly cleaned by running in 45-50 cc. of water, shaking and allowing the water to run off and following this by the addition of about 50 cc. concentrated sulfuric acid, washing the mercury with this acid by tilting until the mercury is quite clean. A final washing of the mercury is advisable, the water being carefully removed.

It will be noticed that after some weeks' use, the mercury in the reservoir also requires cleaning and this is effected by shaking it in a separate funnel with dilute nitric acid followed by filtration through a cornucopia of filter paper with a very fine orifice. The glass tap in the decomposition tube should also be frequently cleaned and regreased, the sulfuric acid being washed out with water and the old grease removed with tissue paper. It is stated that a grease made from pure black rubber dissolved in vaseline and, if necessary, with a little paraffin wax, is quite suitable for this purpose.

Determination of Nitrogen with the Gas-Volumeter.¹ By means of this apparatus, the calculations necessary in the nitrometer are obviated, no reference tables being required, the method being applicable for absolute as well as relative measurements. The following description of this apparatus, which was devised and perfected by G. Lunge, is taken from Lunge's *Technical Methods of Chemical Analysis*, substantially in the words of the inventor. By means of this apparatus, the reduction of a volume of any gas, either wet or dry, to normal conditions, (usually 0° and 760 mm. pressure), is effected without observation of the temperature and pressure.

The principle of the apparatus is to enclose a known volume of air at such a pressure that it occupies exactly the volume which it would take up at 0° and 760 mm. pressure. If the same temperature and pressure are now applied to another volume of gas,

1. G. Lunge, *Ber.* 1888, **21**, 376; 1890, **23**, 440; 1892, **25**, 3157; *Zts. ang. Chem.* 1890, **3**, 139; 1891, **4**, 197, 410; 1892, **5**, 677; *J. S. C. I.* 1882, **1**, 15; 1885, **4**, 447; 1888, **7**, 232; 1890, **9**, 547; *Dingl. Poly.* 1879, **233**, 63, 75, 155, 235.

this will also occupy the volume which it would take up at 0° and 760 mm. pressure. This condition is brought about by confining the known volume of air in a "reduction tube," to which a pressure tube is attached, and placing the latter in such a position that the gas in the reduction tube is brought to the volume it would occupy under normal conditions. The reduction tube being connected to the gas-measuring apparatus by means of a T-tube, by adjusting the level of the mercury in the two tubes to the same height, the volume correction is applicable directly to the gas in the measuring tube.¹

The apparatus, which consists of two sections, is shown in Fig. 84, the three tubes *A*, *B* and *C*, being connected as indicated with sufficiently long rubber tubing (so-called "pressure tubing"), each tube being held in position by movable clamps working vertically. The measuring tube *A* may be a nitrometer or any other gas-measuring apparatus. The so-called reduction tube *B*,

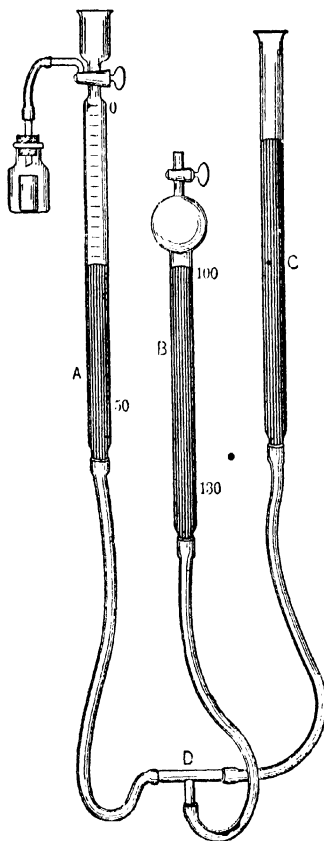


FIG. 84.—LUNGE GAS-VOLUMETER

1. A little experience will enable adjustment to be made with accuracy. It must be remembered that the acid portion above the mercury has a density of about 1.8, while that of the mercury is about 14. Therefore, when comparing the heights of mercury in the two tubes, the mercury in the pressure tube should be raised higher than the mercury in the measuring tube, by about $\frac{1}{2}$ of the height of the acid in the latter tube. According to R. Kaesbohrer (Chem. Ztg. 1918, **42**, 296; abst. J. C. S. 1918, **114**, ii, 273; C. A. 1918, **12**, 2297), a more trustworthy procedure is to bring the mercury to the same level in the measuring and leveling tubes, read the volume of the gas, open the tap of the measuring tube, and note the difference of the mercury. This difference in mm. is subtracted from the barometric pressure during the de-

is either enlarged at the top, or preferably as shown,¹ of cylindrical form in order to bring the inclosed volumes of gas as far as possible into a parallel position. The first graduation indicates a volume of 100 cc., the lower cylindrical portion being divided into 0.1 cc. for another 30–40 cc. The tube is set once for all, by observing the temperature and pressure, calculating the volume which 100 cc. of dry air would occupy under the observed conditions, bringing the mercury to the corresponding division, and closing the tap above the bulb.² The pressure tube *C* is preferably constricted at the bottom as shown in *B* in order to economize the amount of mercury needed to fill the system.³

When any gas-volumetric operation has been carried out in *A* the volume of gas is now read in the ordinary manner after adjusting the mercury in *A* and *C* to equal levels. Before taking the reading of the volume of gas in *A*, the three tubes are so adjusted that the mercury in *B* stands at the 100 cc. graduation, and the levels in *A* and *B* are the same.⁴ This adjustment is most readily carried out in the following manner: The tube *A* is securely clamped while *B* and *C* are raised, *C* to such an extent that the mercury in *B* rises to the graduation 100 cc. *B* and *C* are then lowered simultaneously, so that the difference of level of the mercury in the two tubes is maintained until the mercury stands at equal levels in *A* and *B*, in the latter still at the 100 cc. graduation.⁵ It is obvious from the above that by the use

termination. Another method of adjustment is by very slightly opening the tap on the measuring tube after first adding a little sulfuric acid in the tap. When accurately adjusted the acid should neither rise nor fall.

1. H. Göckel (Zts. ang. Chem. 1900, **13**, 961, 1238) has devised a tap which is ridged horizontally and sealed by mercury, which Lunge states is satisfactory and generally applicable.

2. If the tap is air-tight, the determination, once made, is permanent. As an alternative, the upper end of the tube may end in a capillary, which can be sealed off after the volume has been correctly adjusted.

3. If moist gases are to be measured in the measuring tube, a small drop of water must be introduced into the reduction tube; if dry gases such as nitric oxide generated over sulfuric acid in the ordinary nitrometer are to be measured, a drop of conc. sulfuric acid is introduced into the reduction tube, but never in sufficient amount to more than cover the top of the mercury meniscus. The gases must be measured either quite dry or saturated with moisture.

4. The gas volumes in *A* and *B* then correspond to such temperatures and pressure that their volumes are equal to those which they would occupy when dry at 0° and 760 mm. pressure, since this condition (if properly conducted) is insured once for all in the case of *B*, and the gas in *A* is at the same temperature and under the same pressure.

5. Usually the adjustment will be found a trifle inexact, which can be

of the gas-volumeter all thermometric and barometric readings, and all reductions by calculation or special tables, are avoided; the volume of gas is read off directly under conditions corresponding to the normal pressure and temperature. As it is not easy to shake the mercury and sulfuric acid in the tube itself when a reduction tube is attached, and as there is danger of the gas going over into the reduction tube, it is advisable to induce the decomposition in a separate apparatus, *E* and *F*, Fig. 85, and then transfer to the volumeter for measurement. *E* is the reaction vessel of capacity of about 100 cc. when used for the analysis of nitrous vitriol, and of about 200 cc. when used for the analysis of dynamite and nitrocellulose. It is provided with a tap, a beaker *c*, and pressure tube *F*, arranged as in the ordinary nitrometer.¹ To carry out a determination *F* is first raised until the mercury reaches the end of the capillary *a*, which is then closed with a ground glass or rubber cap *b*, to prevent the escape of mercury on shaking, and the tap *E* also closed. The material to be determined is introduced in the usual manner through the cap *c*, the reaction induced by shaking, and the whole allowed to stand to regain atmospheric temperature. *E* and *A* are then brought to the same height, as shown in the figure, and the mercury in the measuring tube of the volumeter *A* driven over to the end of the thick rubber tube attached to the capillary *d*. The cap *b* is then removed, the capillary *a* slipped into the rubber connecting tube until glass touches glass, *F* raised and *C* lowered, the two connecting taps opened, and the gas siphoned from *E* to *A*. The tap on *A* is closed as soon as the acid from *E* reaches the bottom of the capillary tube *e*. The levels in *A* and *B* are then adjusted, and the mercury in *B* brought to the 100 cc. graduation, as described above.² By use of several reaction vessels, many

remedied by a slight movement of *B*. In cases where another liquid is introduced into the measuring tube besides mercury, the pressure which it exerts must be taken into account. For instance, in nitrogen determinations by the Dumas method, a mark is made below the 100 cc. graduation of the reduction tube, corresponding to one-tenth the height of the potassium hydroxide solution in the measuring tube, the sp. gr. of which may be taken as $\frac{1}{10}$ that of the mercury. In then reading off the volume of nitrogen,

the mercury in the reduction tube is brought to the 100 cc. graduation, and that in the leveling tube to the special mark below, by which means the height of the potassium hydroxide solution is allowed for.

1. *E* is best supported by a ring, and *F* by a clamp.

2. This method of transferring gas is advantageous, not only because

more determinations can be carried out in a given time than is possible with the ordinary nitrometer.

Determination of Nitrogen by Du Pont Nitrometer. This instrument¹ (see Fig. 85) consists of six glass parts as follows: A globe-shaped reservoir (*a*); a generating bulb (*b*) of about 300 cc. capacity, the generating bulb having stopcocks at both top and bottom to permit a violent agitation, and having a cup above which communicates with the bulb through the upper stopcock; a second globe-shaped reservoir (*c*), to which, by means of a glass multiple connecting tube and rubber tubing, are joined a compensating burette (*d*), a reading burette (*e*), and an additional measuring burette (*f*). The reading and compensating burettes are of the same shape and size, and are blown out into bulbs at the top. The compensating burette is not graduated. Above the bulb it has a small vertical open tube, which is sealed when the instrument is standardized. The reading burette is calibrated so that percentages of nitrogen may be read therefrom, and is marked to read from 10% to 14%, being graduated to one-hundredths of 1%. Between 171.8 cc. and 240.4 cc. of gas must be generated to obtain a reading; that is, the 10% mark represents the volume of 171.8 cc. of NO at 20° and 760 mm. pressure, containing 0.1 gm. of nitrogen; the 14% mark is equal to 240 cc. NO under the same conditions, representing 0.14 gm. nitrogen.

The compensating burette is supported by a ring; the generating bulb is supported just above each stopcock by forked holders, curved so as to retain the bulb in place. In order to remove the generating bulb it needs only to be raised slightly and brought forward, the manipulation of a screw, as with the the pressure due to the sulfuric acid does not have to be allowed for, but also because the unavoidable dirtying of the apparatus is confined to the reaction vessel *E*, which is readily cleaned. Care should be taken that the bores of the capillaries *a* and *d* are not enlarged at the ends, so that no bubbles of gas will adhere upon connecting up. M. Sanders concludes (J. Ind. Eng. Chem. 1920, **12**, 169; abst. C. A. 1920, **14**, 710) that results accurate to 0.1% cannot be obtained with the nitrometer if the sample contains more than 15%-17% NaCl on a dry basis. See B. Davisson and J. Parsons, J. Ind. Eng. Chem. 1919, **11**, 306; abst. C. A. 1920, **14**, 711.

1. This description is taken from Technical Paper 160, U. S. Bur. Mines, by W. Cope and G. Taylor. See also, W. Snelling and G. Storm, Bull. 51, Bur. Mines. J. Pitman, J. S. C. I. 1900, **19**, 983. G. Lunge, J. S. C. I. 1901, **20**, 100. C. Hill, Analyst, 1918, **43**, 217; abst. J. S. C. I. 1918, **37**, 413-A.

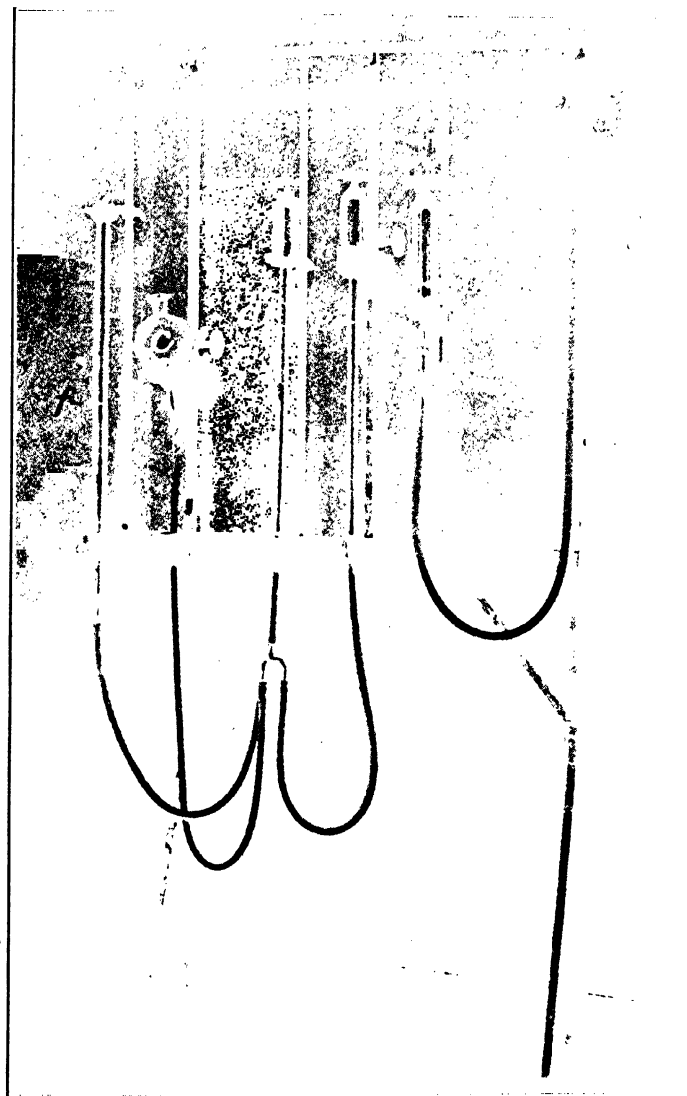


FIG. 85.—DU PONT NITROMETER

ordinary clamp, thus being avoided. The two reservoirs and the reading burette are supported by ring clamps, these clamps having milled rollers at the shank; they are moved up and down vertical racks by means of hand screws, the rollers being so arranged in conjunction with the vertical racks that the weight of the part presses them down and acts as a brake, thus preventing their moving when not being manipulated.

Having arranged the apparatus and filled the compensating, reading and generating tubes as well as their connections with mercury, the next step is to standardize the instrument. Twenty to thirty cc. of sulfuric acid are run into the generating bulb through the cup at the top, and at the same time about 210 cc. of air is let in; the cocks are then closed and the bulb well shaken; this shaking thoroughly desiccates the air, which is then run into the compensating burette until the mercury is about on a level with the 12.50% mark on the reading burette, the two burettes being held at the same height. The compensating burette is then sealed off at the top. A further quantity of air is desiccated in the same manner and run over into the reading burette until the height of mercury in the reading burette stands at about the 12.50% mark. The cocks are then closed, and a small piece of glass tubing, filled with sulfuric acid (not water), and bent in the form of a U, is attached to the outlet of the reading burette. When the mercury columns are about balanced and the inclosed air has been cooled to room temperature, the cock is again carefully opened and when the sulfuric acid balances in the U-tube, and the mercury columns in both burettes are therefore in the same level, the air in each tube is subject to the same conditions, namely, atmospheric temperature and pressure. A reading is now made from the burette, and barometric pressure and temperature are carefully noted. Using the well-known formula

$$V = \frac{V'P'(273 + t)(1 - 0.00018 t')}{P(273 + t')(1 - 0.00018 t)}$$

the volume this enclosed air would occupy at a pressure (P) of 29.92 inches of mercury (760 mm.) and at a temperature (t) of 20° is determined. The cock is again closed and the reservoir and reading burette carefully adjusted so as to bring the air in the reading burette to the calculated volume and the mercury

in the compensating burette to the same level as the mercury in the reading burette. A strip of paper is now posted on the compensating burette at the level of the mercury and the standardization is then complete.

There is, however, another and shorter method of standardization than the one described above. It is well known that the quality of the sulfuric acid used in the nitrometer will materially affect the results. To ascertain whether sulfuric acid is suitable for use in making nitrogen determinations in the nitrometer a determination is made on chemically pure dry potassium nitrate and the reading obtained in the nitrometer is compared with the theoretical percentage of nitrogen in potassium nitrate. In applying this procedure to the standardization of the nitrometer the compensating burette is filled with desiccated air, as described above, and 1 gm. of potassium nitrate, dissolved in 2 cc. to 4 cc. of water, is introduced into the generating bulb, the cup is washed with 20 cc. of 95% to 98% sulfuric acid in three or four portions, and each portion is run separately into the bulb. The gas, when generated, is run over into the reading burette, and the mercury columns in both burettes are leveled, so that the mercury in the reading burette is also at 13.86, the theoretical percentage of nitrogen in potassium nitrate. A strip of paper is pasted on the compensating burette at the level of the mercury, and the standardization is accomplished.

This method of standardizing offers many advantages over that first described among which may be mentioned that no readings of temperature or pressure are necessary. Probably the greatest advantage is that if the acid used in standardizing should contain impurities, which might otherwise affect the result, the error is entirely compensated and corrected in subsequent work; that is to say, the instrument having been so standardized that the reading gives the theoretical percentage of nitrogen in potassium nitrate, the results will be accurate when testing other substances so long as the same quantity of sulfuric acid from the same lot is used.

It must, of course, be understood that once having standardized the instrument with a certain lot of acid no different lot of acid can be used without re-standardizing. In order to avoid slight differences in results due to variations in the acid, it is advisable

to reserve a sufficiently large uniform stock of acid—for example, a carboy full—for nitrometer use.

The additional measuring burette, with which this type of nitrometer is provided, known as the "universal tube" (f, Fig. 85), is simply a straight burette, marked to read from 0 to 100 in percentages and graduated to one-tenth of 1%. The tube is of such size that 0.30 gm. of NO (or $\frac{1}{100}$ gm.-molecule of NO) under standard conditions of temperature and pressure (26° and 760 mm. pressure) fills it to the 100 mark.

If it is desired to read the percentage of nitrogen direct, 0.14 gm. of substance is weighed out. Consequently, if 1.011 gm. of potassium nitrate, 0.63 gm. of nitric acid, or 0.85 gm. of sodium nitrate are used, the results can be read directly as percentages of the original substance.

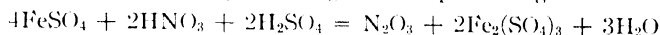
This method is convenient when it is not certain that the reading will fall within the limits of the graduations in the ordinary measuring burette.

The "universal tube" is found particularly advantageous when, for example, the amount of nitroglycerol in a sample is so small that the volume of gas generated is insufficient to fill the large reading burette to its graduated portion. The volume of gas generated from any amount of nitroglycerol up to about 0.75 gm. may be read in the "universal tube." Readings in this measuring tube can be as accurately made as in the regular reading burette.

The sample is weighed into a small beaker and dissolved in 5 to 10 cc. of sulfuric acid with a specific gravity of 1.84 (inorganic nitrates may be previously dissolved in as little water as possible) and transferred to the generating bulb. The beaker and the cup of nitrometer are rinsed several times with acid, the washings being rinsed into the bulb. By lowering the leveling bulb and gently shaking NO begins to be evolved. When all but 60 to 75 cc. of mercury has run out of the generating bulb, the bottom stopcock is closed and the bulb shaken violently three to five minutes. The gas is then transferred to the reading burette, the levels adjusted, and the reading obtained. Care must be taken not to use samples that are too large or too small to fall within the range of the graduations on the burette.

Estimation of Nitrogen by Ferrous Ammonium Sulfate. This

method described by F. Bowman and W. Scott¹ is based upon the fact that nitric acid or a substance containing it, when titrated with a ferrous sulfate solution is oxidized by the acid, and when an excess of ferrous iron is present, combination with the reduced nitrogen compounds takes place, with the formation of a red compound, which red compound indicates the end point of the reaction. The following equation is given as representing the reaction:



Ferrous ammonium sulfate, however, has in general been found more suitable than ferrous sulfate owing to the fact that an acid solution of the latter deteriorates less rapidly.²

In preparation of the solution, 50 gm. of ferrous ammonium sulfate are dissolved in 400 cc. distilled water, and when solution is complete 500 cc. of cold 50% sulfuric acid is poured into the solution with thorough stirring during addition of the acid. The liquid is then cooled and diluted to one liter with distilled water. A further liter of dilute sulfuric acid as before is then added and the liquid thoroughly mixed. The strength of this solution is varied according to the use for which it is intended. The above strength of solution, however, has been found suitable for the estimation of nitric acid in niter cake, although a more concentrated solution is preferable for the determination of nitrogen in cellulose nitrate. For this latter purpose 500 gm. ferrous ammonium sulfate are weighed out and the solution made up as above described.

In standardizing the solution, approximately 100 cc. of concentrated sulfuric acid are run into a 250 cc. titration flask with 10 cc. of standard solution of potassium nitrate of strength equivalent to 10 millimeters of nitric acid per cc. of solution, the above being added by means of a pipette. The ferrous ammonium sulfate solution is then run in from the burette, the end point of the titration being indicated by a faint pink coloration which is permanent. It is advisable that the temperature of the liquid be kept below 30° during the titration. Assuming that 10 cc. of standard KNO_3 solution require X cc. ferrous ammonium sulfate solution, then

1. J. Ind. Eng. Chem. 1915, **7**, 766; abst. C. A. 1915, **9**, 2747; J. S. C. I., 1915, **34**, 1008.

2. Where nitric and nitrous acids are both present, the nitric acid alone is determined by this method, the results being identical with those found by the nitrometer.

$\frac{0.01}{X}$ gm. will represent the HNO_3 equivalent of one cc. of the solution.

In the determination of nitrogen in cellulose nitrate from 1.0–1.1 gm. pure, finely ground KNO_3 is weighed into a capsule, dried in an air oven at a temperature of 110° – 120° for two hours, and after cooling in a desiccator, accurately weighed. 150 cc. concentrated sulfuric acid is then measured into a dry 500 cc. flask and the potassium nitrate carefully added, any crystals adhering to the sides of the flask being washed down with sulfuric acid. The weighing bottle is then reweighed and the weight of the potassium nitrate used obtained by difference. When solution of the salt in the sulfuric acid is complete, ferrous ammonium sulfate solution is slowly run in from a burette until a permanent red coloration results. As before, the temperature should be kept below 30° . As one gm. of KNO_3 equals 0.1385 gm. N, the strength of the solution expressed in terms of grams—nitrogen per cc. is as follows:

$$\frac{\text{Wt. of } \text{KNO}_3 \text{ taken} \times 0.1385}{\text{cc. of ferrous solution used}}$$

This method can be advantageously employed for estimation of nitrogen in ferrous substances as follows:

Determination of Nitric Acid in Niter Cake by Ferrous Ammonium Sulfate. 5 gm. of the niter cake are dissolved in 20 cc. of water and 100 cc. concentrated sulfuric acid added. The solution is then titrated with standardized ferrous ammonium sulfate solution as described above, the percentage of HNO_3 present in the sample being calculated by the formula:

$$\frac{X \times Y \times 100}{W}$$

Where $X = \text{HNO}_3$ equivalent to 1 cc. of the ferrous ammonium sulfate solution

$Y = \text{cc. of solution used in the titration.}$

$W = \text{weight of niter cake taken.}$

Estimation of Nitrogen in Nitrocellulose by Ferrous Ammonium Sulfate.¹ Cellulose nitrate is first dried in the oven to con-

1. Best results are to be obtained by adding the nitrocellulose to the cold mixture of ferrous solution and sulfuric acid, for the determination

stant weight and then comminuted by rubbing through a 10-20 mesh sieve, approximately 1.1-1.2 gm. being weighed into a weighing bottle, dried, cooled and re-weighed. 150 cc. concentrated sulfuric acid are then measured into a 500 cc. flask and 20 cc. of ferrous ammonium sulfate solution run very slowly into the flask, the mixture being kept cool as before suggested. The nitrocellulose is then quickly transferred to the flask and the weighing bottle re-weighed in which the total weight of cellulose nitrate used, is determined. The percentage of nitrogen in the nitrocellulose is then calculated by the formula:

$$\frac{X \times Y \times 100}{W}$$

Where X = Nitrogen equivalent to one cc. of the ferrous ammonium sulfate solution

Y = cc. used in the titration

W = weight of nitrocellulose taken.

Under the conditions of manipulation as above described, one experienced with the reaction should have no difficulty in obtaining results which compare favorably with that of the nitrometer.

Determination of Nitric Acid by Nitron. A gravimetric method for determining nitric acid by precipitation as nitron nitrate has been worked out, and while the determination of free or combined nitric acid volumetrically is usually preferable, isolation of nitric acid as nitron nitrate ($C_{20}H_{16}N_4.HNO_3$) may occasionally be used. The fairly insoluble, crystalline compound is formed by the addition of the base diphenyl-endo-anilo-hydro-

requires some two hours when carried out wholly in the cold. Where the nitrocellulose is added to a *warm* solution the reaction proceeds too vigorously.

L. Mauge (l'Ind. chim. 1918, **5**, 255; abst. C. A. 1919, **13**, 545) has studied this method critically. He obtains best results by preparing a standard solution containing 66.66 gm. $FeSO_4.7H_2O$ per liter. Into a glass provided with a foot base, measure 100 cc. of the ferrous solution, and add, with shaking, 50 cc. sulfuric acid, 60°-66° Bé. Add from a burette the mixture to be examined. Shake constantly and add the solution to be examined gradually, depending on the HNO_3 content. The brown coloration first formed, becomes nearly black, and then is suddenly discharged. To prepare the standard solution, dissolve 67 gm. crystallized $FeSO_4.7H_2O$ in one liter of water. Titrate with $KMnO_4$ and calculate the dilution necessary to bring the exact concentration to 66.66 gm. per liter. Stabilize by adding about 10 cc. H_2SO_4 to the solution. A layer of paraffin oil is useful to protect the solution from the air, but in any event it must be frequently prepared. He has given graphs to assist in making rapid calculations.

triazole (nitron) to the solution containing the nitrate.

The reagent is prepared by dissolving one part of nitron in nine parts of 5% acetic acid with the aid of heat, filtered and preserved in dark bottles. Inasmuch as the solution does not keep well, it is best prepared in small quantities.

To a solution of the nitrate, containing preferably 0.10 to 0.15 gm. in 80 cc. of solution, 12 to 15 drops of dilute H_2SO_4 is added. This mixture is heated to the boiling point and 12 to 15 cc. of the nitron reagent added, then it is stirred and let stand one-half to three-fourths of an hour. Long, silky needles separate on cooling. The beaker is placed in ice water for 1 to 2 hours and the contents filtered on a Munroe or Gooch crucible, being washed with ice water, 1 or 2 cc. at a time, and not more than 10 cc. in all. A portion of the filtrate may be used to clean the beaker. The precipitate is dried at 105° to 110° ; an hour usually being sufficient. To insure complete precipitation, a little more reagent is added to the heated filtrate and cooled as before. The molecular weight of nitron nitrate is 375.2; the nitrogen factor is therefore 0.03734. Of the compound, 16.53% is NO_3 . 100 cc. water dissolves 0.0099 gm. nitron nitrate.

A modification for nitrocellulose has also been found to be accurate.¹ In one test 0.2 gm. of the sample of nitrocellulose was heated on a steam bath with 5 cc. of a 30% solution of NaOH and 10 cc. of 3% hydrogen peroxide (H_2O_2) solution until frothing ceased and solution was nearly complete. Complete solution was effected by boiling. Then 10 cc. of water and 10 cc. of peroxide were added and the whole heated on a steam bath to a temperature of about 50° and 40 cc. of a 5% H_2SO_4 solution was delivered from a pipette to the bottom of the mixture. The acid was mixed with the solution, which became acid in reaction, and the mixture heated to 80° , when the nitron reagent was added. From this point the procedure was the same as for inorganic nitrates. The results showed 13.13% and 13.11% nitrogen, as compared with 13.15% obtained with the nitrometer.

The filtrate and washings are made slightly alkaline with ammonia and the precipitated nitron washed with water. The nitron nitrate precipitates are added to dilute ammonium hy-

1. For precipitation of nitric acid as hexamethylenetetramine nitrate, see Zentralst. f. wiss. tech. Unters., D. R. P. 298412, 1916; Abst. J. S. C. I. 1919, 38, 925-A.

droxide, warmed to 60°, and the nitron filtered quickly, washed with cold water and dried in a vacuum. Decomposition may be avoided by conducting the operation in an atmosphere of inert gas and as much as possible away from light.

Determination of Nitric Acid by Titration.¹ The specific gravity is determined by a calibrated hydrometer with thermometer attachment, and reduced to normal temperature and pressure.

The total acidity is determined by titration with *N*.NaOH, using methyl orange as indicator. For the concentrated acid, 2.5-3 gm. are accurately weighed in a weighing capsule or oleum bulb, which is then dropped into a titration flask containing 100-150 cc. water, under which it is broken, care being taken to see that all the acid has been washed out of the capillaries of the bulb. *N*.NaOH is then run in from a burette until the end of the reaction is approached, after which one or two drops of a 0.1% solution of methyl orange is added. Due to the fact that methyl orange is destroyed by nitrous acid, it is advisable to add the indicator towards the end of the titration only. The burette is allowed to drain two or three minutes after the end reaction has been obtained, and the reading taken. Temperature and calibration corrections are then applied, and the result calculated as nitric acid.²

Determination of Nitrous Acid by Permanganate by titration against *N*.2 KMnO₄. Ten cc. of the permanganate solution are pipetted into a flask containing 100 cc. water to which a few drops of sulfuric acid has been added. The temperature is maintained between 20°-40° while the acid to be analyzed is being run in, the end reaction being taken when a faint pink coloration persists for at least one minute.

The amount of nitric acid is obtained by subtracting the nitrous acid expressed as nitric acid from the total acid calculated as HNO₃. See analysis of Mixed Acids in Chapter VII of this

1. For standard alkali for mixed acid control, and the standardization of alkali against acid potassium phthalate, see F. Dodge, *J. Ind. Eng. Chem.* 1915, **7**, 29; abstr. C. A. 1915, **9**, 277. W. Hendrixson, *J. Amer. Chem. Soc.* 1915, **37**, 2352. H. Cowles, *J. Amer. Chem. Soc.* 1908, **30**, 1192; abstr. C. A. 1908, **2**, 2355. E. Hearsey and C. Joyce, *J. Ind. Eng. Chem.* 1919, **11**, 341; abstr. C. A. 1919, **13**, 1062.

2. R. Cook (*Chem. Analyst*, 1917, **22**, 18; abstr. C. A. 1918, **12**, 642) has described a convenient pipette for fuming acids.

volume for details of the various methods usually employed.

Manufacture of Absolute Nitric Acid. The Salpetersäure Industrie Gesellschaft¹ prepare nitric acid of 100% concentration by electrolysis, the nitrogen oxides formed at the cathode being introduced at the anode and there oxidized by the nitrogen formed into HNO_3 after having been liquefied by refrigeration. They also advocate² the employment of waste acid from nitrating processes for the anodic liquor in the above process.³

In the M. Moest process⁴ for concentration, nitric acid is prepared by treating aqueous nitric with the gases of liquid NO_2 sufficient to produce nitrification and thus oxidizing oxygen. The layers are subsequently separated from each other and the NO_2 removed and re-used.

L. Friderich⁵ acts upon a molecular mixture of liquid nitrogen peroxide and water with oxygen under pressure or, instead of nitrogen peroxide, the material produced by absorbing N_2O_4 by wood or charcoal may be employed.⁶

J. Douzal⁷ claims to obtain nitric acid of high concentration direct from nitrous substances by converting the nitrous acid into direct acid as it is formed, and preventing the formation of NO_2 by subjecting the nitrous vapors before the hydration to a temperature of 24° , in the presence of an amount of water strongly charged with ozone. In the processes devised by the Elektro-

1. D. R. P. 180052; abst. Mon. Sci. 1909, **71**, 74; Chem. Zentr. 1907, **78**, I, 1083; Chem. Ztg. Rep. 1907, **31**, 86; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1906, **52**, I, 446; Zts. ang. Chem. 1907, **20**, 1329; Zts. Schiess. Spreng. 1907, **2**, 35.

2. D. R. P. 180587; abst. Mon. Sci. 1909, **71**, 159; Chem. Zentr. 1907, **78**, II, 115; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1907, **53**, I, 419; Zts. ang. Chem. 1907, **20**, 1196; Zts. Schiess. Spreng. 1907, **2**, 55.

3. D. R. P. 184958; abst. Mon. Sci. 1907, **71**, 160; Chem. Zentr. 1907, **78**, II, 649; Chem. Ztg. Rep. 1907, **31**, 309; Jahr. Chem. 1905-1908, I, 1767; Wag. Jahr. 1907, **53**, I, 387; Zts. ang. Chem. 1907, **20**, 1195.

4. U. S. P. 1180061, 1916; abst. J. S. C. I. 1916, **35**, 635; C. A. 1916, **9**, 1581; Chem. Ztg. Rep. 1917, **41**, 124. E. P. 4345, 1915; abst. J. S. C. I. 1916, **35**, 537; C. A. 1916, **9**, 2432. Swed. P. 40600, 1916; abst. C. A. 1916, **9**, 2391.

5. E. P. 319, 1911; abst. J. S. C. I. 1911, **30**, 684; Chem. Ztg. Rep. 1911, **35**, 392; C. A. 1911, **5**, 3136. The process is carried out in an autoclave provided with a stirring apparatus, liquid peroxide being first introduced and water added in small quantities at a time. Oxygen under pressure is then forced in.

6. E. P. 403, 1911; abst. C. A. 1911, **5**, 3136; J. S. C. I. 1911, **30**, 684; Chem. Ztg. Rep. 1911, **35**, 392.

7. F. P. 396387, 1908; abst. C. A. 1911, **5**, 357; Mon. Sci. 1910, **73**, 161; Chem. Ztg. Rep. 1909, **33**, 279.

chemische Werke,¹ solutions of nitrogen pentoxide and monohydrated nitric acid are first obtained by the electrolysis of solutions of N_2O_4 or N_2O_5 in HNO_3 . A solution of this nature results in 20% N_2O_5 . A solution of 17 parts N_2O_4 in 80 of HNO_3 is placed in the anode still and electrolyzed with platinum anodes at a current density of 200 amperes per meter.

Valentiner & Schwarz² are of the opinion that the reason why 100% nitric acid had not been prepared before the disclosure of their patented process was the difficulty of decomposing the sodium nitrate by sulfuric acid of sp. gr. 1.85 in a vacuum on a large scale owing to the enormous amount of foam which inevitably forms upon the addition of the acid, and especially at the middle of the operation, and the unavoidable carrying over of acid sodium sulfate. This frothing, however, may be greatly minimized by adding the sulfuric acid in small amounts at a time, the retort being charged with the sodium nitrate and with not over one-third of the amount of sulfuric acid to be used, the remaining two-thirds being introduced in portions during a period of one-half to one hour's time after heat has been applied. The amount of sulfuric acid going into the retort is gauged by the speed of distillation and is calculated at such rate that there is always sufficient sulfuric acid present to decompose the nitrate into bisulfate and nitric acid. Sulfuric acid may advantageously be introduced by being run into the retort neck through a vessel filled with pumice stone through which the nitric acid vapors are caused to pass before leaving the retort and in this manner they are further purified and concentrated.

F. Winteler³ deduces the following points for obtaining nitric acid of the highest concentration and maximum yield: 1st, the temperature of distillation is held as low as possible consistent with running off the charge in an economical period of time; 2nd, the contents of the retort must be uniformly heated and special

1. E. P. 15432, 1911; abst. J. S. C. I. 1911, **30**, 1251; C. A. 1913, **7**, 27. D. R. P. 231546; abst. Mon. Sci. 1915, **82**, 56; Chem. Zentr. 1911, **82**, I, 767; Chem. Ztg. Rep. 1911, **35**, 111; Chem. Zts. 1911, **10**, No. 2501; Wag. Jahr. 1911, **57**, I, 471; Zts. ang. Chem. 1911, **24**, 565; Zts. Schiess. Spreng. 1911, **6**, 157. See Chem. News, 1869, **20**, 285; 1906, **93**, 78.

2. D. R. P. 144633; abst. Mon. Sci. 1904, **61**, 81; Chem. Centr. 1903, **74**, II, 694; Chem. Ztg. 1903, **27**, 880; Chem. Zts. 1904, **3**, 148, 164; Jahr. Chem. 1903, **56**, 382; Wag. Jahr. 1903, **49**, I, 337; Zts. ang. Chem. 1903, **16**, 898. See F. Valentiner, U. S. P. 920224, 1909.

3. Chem. Ztg. 1905, **25**, 820, 1010.

care observed in not over-heating at any particular place, and this is avoided by the slow and uniform application of the heat; 3rd, nitric acid of highest concentration and maximum yield is not insured by the employment of highly concentrated sulfuric acid and previously dried sodium nitrate, but rather with sulfuric acid of about 92%; 4th, the yield of concentrated nitric acid is increased by keeping an abundant supply of atmospheric oxygen in the retort; 5th, to avoid loss it is advocated to cool the distilling gases as quickly as possible.¹

Refinement and Bleaching of Nitric Acid. The refinement of nitric acid by bleaching comprizes driving off the lower oxides in order that the acid may be rendered substantially colorless. This is accomplished quickly by blowing a current of air through the acid, gently heated air together with the gases contained in it being led through a small coke tower fed with water, where dilute nitric acid is obtained, or the gases may be led into a system of tourelles in a manner similar to the condensation of weak nitric acid. This refining, while unnecessary for nitric acid used in the manufacture of sulfuric acid, is, however, required for nitric acid intended for the nitration of cellulose.

C. Casman² refines and bleaches nitric acid by passing a strong current of air through heated nitric acid in order to oxidize the lower nitrogen oxides into the dioxide which is subsequently oxidized into nitric acid by means of a jet of air and steam.

In the German patent of R. Hirsch,³ the impure acid is first led through a stoneware worm which is heated by placing in water at 80° to 90°, air being blown in at the bottom, the amount of nitric acid fed in being so arranged that it runs out at the bottom at a temperature around 60°, by which means it is said to be completely bleached.

In the manufacture of nitric acid by the Griesheim process there is no necessity for bleaching the acid, as the latter is directly produced in this process in the pure state. The Chemische

1. See also O. Guttmann, Chem. Ztg. 1905, **29**, 934.

2. E. P. 11296, 1913; abst. C. A. 1914, **8**, 3621; J. S. C. I. 1914, **33**, 750. F. P. 457800; abst. C. A. 1914, **8**, 2040; Mon. Sci. 1914, **81**, 13; Chem. Ztg. Rep. 1914, **38**, 103.

3. D. R. P. 46096; abst. Ber. 1889, **22**, 152; Chem. Centr. 1889, **60**, I, 688; Jahr. Chem. 1889, **42**, 2651; Wag. Jahrb. 1889, **35**, 456. See J. Pratt, E. P. 14173, 1884. G. Mowbray, U. S. P. 94969, 1869. J. Waldbauer, Belg. P. 167376, 1902.

Fabrik Griesheim¹ interposes between the nitric acid retort and the storage tank a reflux cooler comprizing a Kohrman's stone-ware worm immersed in a water bath at about 60°. The ascending acid vapors are thereby partially cooled, but as the result of the high temperature, the lower nitrogen oxides, together with small amounts of chlorine, are not condensed, but are further liquefied in the plate tower to weak nitric acid.

E. Schaller² has found in commercial fuming nitric acid from 7.5% to 13.7% of lower oxygen oxides calculated as N_2O_3 , and from five-eighths to 8.1% sulfuric acid.

Concentration of Nitric Acid.³ As far back as 1866, I.

1. D. R. P. 59099; abst. Mon. Sci. 1892, **40**, 176; Ber. 1892, **25**, 223, Wag. Jahr. 1891, **37**, 392; Zts. ang. Chem. 1891, **4**, 609. W. Dieterle and L. Rohrmann, D. R. P. 85240. P. de Lambilly, D. R. P. 74274, 74275, 78573; abst. Zts. ang. Chem. 1894, **7**, 307; Mon. Sci. 1895, **46**, 120; Ber. 1894, **27**, 682; 1895, **28**, 308; Chem. Centr. 1894, **65**, 11, 224; 1895, **66**, 1, 367; Jahr. Chem. 1894, **47**, 427; Wag. Jahr. 1894, **40**, 110, 463, 464; Zts. ang. Chem. 1894, **7**, 307, 721.
2. Chem. Ztg. 1904, **28**, 591.
3. In connection with the purification and concentration of nitric acid, see L. Rohrmann and G. Streit, D. R. P. 39659. R. Hirsch, D. R. P. 46096. A. Erek, D. R. P. 46724. H. de Chardonnet, D. R. P. 56655; Swiss P. 2123. Chem. Fabrik Griesheim, D. R. P. 59099; E. P. 891, 1891. A. Erourard, D. R. P. 62714. F. Valentiner, D. R. P. 63207; E. P. 610, 1895. A. Vogt and C. Wichmann, D. R. P. 69059 and E. P. 22018, 1891. O. Guttman and L. Rohrmann, D. R. P. 73421; E. P. 22481, 1891; U. S. P. 491481. M. Prentice, D. R. P. 79645; E. P. 6960, 1893; U. S. P. 526116. C. Lehmann and J. Walter, D. R. P. 87982; E. P. 20290, 1896. F. Valentiner, D. R. P. 88321, addn. to D. R. P. 63207; E. P. 19192, 1895. J. Skoglund, D. R. P. 104357; E. P. 22816, 1897; U. S. P. 591087. Chemisch-Fabrik Rhenania, D. R. P. 106962. H. Frasch, D. R. P. 82573; U. S. P. 517098. J. Darling and H. Forrest, D. R. P. 83097; E. P. 5808, 1894; U. S. P. 517001. Verein Chemischer Fabriken, D. R. P. 85042. W. Dieberle and L. Rohrmann, D. R. P. 85240, E. P. 14520, 1894. G. Glock, D. R. P. 110254; E. P. 18897, 1899; Aust. P. 4205, 1900. C. Uebel, D. R. P. 127647; E. P. 3505, 1901. U. S. P. 681085. Valentiner and Schwarz, D. R. P. 144633. Chem. Werke vorm. H. Byk, D. R. P. 208143; E. P. 20366, 1908; Aust. P. 41931; U. S. P. 928545. J. Waldbauer, D. R. P. 155006. H. Niedenführ, D. R. P. 155095; E. P. 4353, 1905; Aust. P. 23234, 1905; E. P. 351742. Chemisch-Fabrik Griesheim-Elektron, D. R. P. 170532. Salpetersäure Industrie-Gesellschaft, D. R. P. 180052; E. P. 18603, 1906; Swiss P. 37900; Aust. P. 28680. O. Boeters and R. Wolfenstein, D. R. P. 189865; E. P. 28449, 1906; F. P. 371797; Aust. P. 34170; U. S. P. 864217. O. Dieffenbach, D. R. P. 174736; Aust. P. 28968. R. Wolfenstein and O. Boeters, D. R. P. 191912, addn. to D. R. P. 189865; Aust. P. 34576; E. P. addn. 8459 to E. P. 371797; C. Uebel, D. R. P. 210803. Chemische-Werke vorm. H. Byk, D. R. P. 217476, addn. to D. R. P. 208143; Swiss P. 45318. F. P. 400305; Aust. P. 43492. E. Brauer, D. R. P. 222680; E. P. 14381, 1910; Aust. P. 47105. F. P. 417166. O. Engels and F. Dürre, D. R. P. 229096. Badische Anilin- und Soda Fabrik, D. R. P. 227377; F. P. 406969. Aktiebolaget Swedisch Nitric Syndicate, D. R. P. 233031; E. P. 10592, 1909; Swiss P. 48703; Aust. P. 43740; F. P. 402079. O. Dieffenbach and C. Uebel, D. R. P. 238370.

Baggs¹ purified and concentrated crude nitric acid by treatment with sulfuric acid, the acid to be purified being placed in a series of 3 vessels similar to Woulfe's bottles in contact with hot or cold sulfuric acid. H. Pauling² makes use of this principle in the

- Saccharinfabrik Akt.-Ges. vormals Fahlberg, List & Co., D. R. P. 267869; E. P. 3264, 1913; F. P. 464561. Aktiebolaget Swedish Nitric Syndicate, D. R. P. 236341; E. P. 10591, 1909; Aust. P. 50652; F. P. 402078. F. deJahn, D. R. P. 252374. H. Schellhass, D. R. P. 241711. Aktien-Gesellschaft der Chem. Produkten-Fab. Pommerens-dorf and G. Schüller, D. R. P. 261634, H. Pauling, D. R. P. 257809; E. P. 22322, 1910; Swiss P. 53245; Aust. P. 48815; F. P. 420803; U. S. P. 1031864. H. Pauling, D. R. P. 274165, addn. to D. R. P. 257809; U. S. P. 1074287; F. P. 461326. A. Nodon, D. R. P. 274346. G. Contard and F. Valentiner, E. P. 4254, 1907; Aust. P. 36792; F. P. 374902; U. S. P. 920224. C. Kaesmacher, E. P. 2382, 1908; F. P. 386783. E. Collett, E. P. 7597, 1913. Chem. Fabrik Griesheim Elektron, E. P. 19986, 1905; Aust. P. 26684; F. P. 358373; U. S. P. 819262. H. Pauling, E. P. 22320, 1910; Swiss P. 53244; Aust. P. 48816; F. P. 420804; U. S. P. 1031865. R. Chatfield, E. P. 16512, 1891. H. Hemingway, U. S. P. 781826; H. Pauling, U. S. P. 887266. H. Blackmore, U. S. P. 982466. E. Brauer, U. S. P. 1008690. R. Sohlanan and C. Lundholm, U. S. P. 1009197. Verein Chemischer Fabriken, F. P. 462290. C. Uebel, E. P. 19881, 1913; F. P. 461452. Salpetersäure Industrie-Gesellschaft, Swiss P. 56360, 57531; Aust. P. 61387. C. Rassi, F. P. 455534, 455532. C. Volz, U. S. P. 500786. J. White, U. S. P. 648322. W. Mills, U. S. P. 755378. I. Moscicki, Aust. P. 38937. E. Collett, F. P. 357221; U. S. P. 854928. Salpetersäure-Industrie, F. P. 368716. Farbwerke vorm. Meister, Lucius and Brüning, F. P. 432990. E. Collett, F. P. 447106. M. Prentice, E. P. 8902, 1893. A. Campbell and A. Walker, E. P. 9782, 1894. W. Garroway, E. P. 2466, 1895. H. Baynes and The Chemical and Elektrolytic Syndicate, E. P. 7273, 1895; U. S. P. 632394. C. Dreyfus, E. P. 13826, 1895. R. Main and W. Donald, E. P. 23819, 1895. W. Garroway, E. P. 6777, 1899. Det Norske Aktieselskab for Elektrokemisk Industrie and B. Halvorsen, E. P. 3680, 1906. F. P. 317544, 323760, 325244, addn. 332 to 317544, 348189, 351742, 354073, 357221, 358373, 363157, 370977, 371797, 374237, 374902, 380121, 385605, 388276, 389059, addn. 8459 to 371797, 396161, 396367, 398738, 400308, 404720, 406806, 406969, addn. 10023 to 374237, 416036, 416224, 417166, 420803, 420804, 423893, 424598, 432990, 433502, 435197.
1. E. P. 3269, 1866. Compare F. de Sussex, E. P. 11585, 1847; 590, 1852; 1649, 2095, 1856. J. Webster, E. P. 2535, 1862. See J. Bouchard-Praciq, F. P. 197358, 1889. In the method of O. Jensen (U. S. P. 1324255, 1919; abst. C. A. 1920, **14**, 454) nitric acid containing nitrogen oxides is passed in countercurrent to nitric acid vapors so that N_2O_4 is expelled and condensed. The acid purified by this treatment is distilled and dephlegmated, producing dilute liquid acid and vapors of highly concentrated acid, and a portion of the latter is passed in countercurrent with the acid to be purified. Another portion is condensed to produce highly concentrated acid.
 2. U. S. P. 887266, 1908; 993868, 1911; abst. C. A. 1912, **6**, 2676; Chem. Ztg. Rep. 1911, **35**, 342; Mon. Sci. 1909, **71**, 113; 1912, **77**, 18. 1031864, 1074287, 1913; abst. C. A. 1912, **6**, 2676; 1913, **7**, 3821. E. P. 22037, 1909; 22320, 22322, 1910; 8533, 1911; abst. J. S. C. I. 1910, **29**, 211; 1911, **30**, 84; 1912, **31**, 231; C. A. 1912, **6**, 2825; Chem. Ztg. Rep. 1911, **35**, 54, 66. F. P. 420803, 420804, 1910; abst. J. S. C. I. 1911, **30**, 284; Mon. Sci. 1913, **79**, 113. F. P. 461326, 1913. Cf. A. Cocking and Kynock, Ltd., E. P. 129305, 129306, 1916; abst. C. A. 1919, **13**, 2978; J. S. C. I. 1919, **38**, 680-A. E. P. Appl. 117, 1918. In their E. P. 130038, 1918, dilute nitric acid is neutralized with ammonia, the resulting solution evaporated to crystallization of ammonium

production of concentrated nitric acid by distilling the dilute acid in the presence of concentrated sulfuric acid or other similarly acting hygroscopic substance, the evaporation of the nitric acid being effected in a columnar or like apparatus by means of a countercurrent of steam, in place of the current of hot gases or the use of external heat. The steam is preferably superheated.

In the concentration of nitric acid (up to monohydrate) according to the process of F. Hausmann,¹ a mixture of nitric and sulfuric acids is passed in a shallow layer over the bottom of a still, while a current of cold air is blown over the surface of the layer, the nitric acid being withdrawn to obtain a product free from nitrous acids or the lower oxides of nitrogen.

In the N. Titlestad method,² the nitric acid is boiled and a mixture of vaporized and liquid acid introduced into a concentrating apparatus where it is treated with a countercurrent of strong sulfuric acid.

O. Jensen,³ has obtained best results by absorbing nitrous nitrate, and the dried salt decomposed at reduced pressure with strong sulfuric acid (preferably waste acid from nitrating plant). See E. P. 3922, 1883; 8902, 1893; 25632, 1907; E. P. 125444.

1. U. S. P. 1115192, 1915; abst. C. A. 1915, **9**, 129. See also N. Niedenführ, E. P. 351742; abst. Mon. Sci. 1906, **65**, 102. A. McDougall, E. P. 4643, 1899; Aust. P. 2805. See also E. I. Du Pont de Nemours Co., U. S. P. 1149711, 1915; abst. J. S. C. I. 1915, **34**, 960; Chem. Ztg. Rep. 1916, **40**, 132.

2. U. S. P. 1178888, 1916; abst. C. A. 1916, **10**, 1581; abst. J. S. C. I. 1916, **35**, 635. E. P. 19792, 1914; J. S. C. I. 1915, **34**, 1053. Other patents by this firm are: U. S. P. 1173699; abst. J. S. C. I. 1916, **35**, 477. U. S. P. 1148343, 1096321; abst. C. A. 1914, **8**, 2120. E. P. 388276, 414925, 425997, 465504, 465739, 466100, 466961, 466962, 475989, 476633, 477726, 480205; abst. C. A. 1914, **8**, 3491, 3492; Mon. Sci. 1909, **71**, 110; 1913, **79**, 121; 1917, **84**, 31; Chem. Ztg. Rep. 1908, **32**, 452; 1914, **38**, 479, 586; J. S. C. I. 1916, **35**, 46, 601; 1917, **36**, 215. D. R. P. 206949; abst. Mon. Sci. 1912, **77**, 90; Chem. Zentr. 1909, **80**, I, 1127; Chem. Ztg. Rep. 1909, **33**, 137; Chem. Zts. 1909, **8**, No. 1184; Jahr. Chem. 1909, **62**, 531; Wag. Jahr. 1909, **55**, I, 417; Zts. ang. Chem. 1909, **22**, 551; Zts. Schiess. Spreng. 1909, **4**, 95. E. P. 100099, 1916; abst. J. S. C. I. 1917, **36**, 214. Aust. P. 55238, Norw. P. 27291, 27450, 1916; abst. J. S. C. I. 1908, **27**, 897; 1909, **28**, 365; 1910, **29**, 1317; 1911, **30**, 1014; 1914, **33**, 601; 1915, **34**, 872, 913, 1053; 1916, **35**, 46, 215, 601; 1917, **36**, 214.

3. U. S. P. 1197295, 1916; abst. J. S. C. I. 1916, **35**, 1260; C. A. 1916, **10**, 2966. J. Davis (U. S. P. 1314485; abst. C. A. 1919, **13**, 2741; J. S. C. I. 1919, **38**, 718-A) employs an apparatus for obtaining concentrated HNO_3 from nitrous gases such as are formed by the oxidation of ammonia. The apparatus comprises a shaft of acid-proof masonry, having in its lower part a series of arches with slots between them and filled above these arches to a depth of several feet with broken quartz or other acid-proof material, leaving considerable clear space in the shaft above the filling. Below the arches is mounted a basin of duriron or other material resistant to the action of strong hot HNO_3 . An overflow pipe leads from the basin to an acid-proof cooler.

gases in concentrated sulfuric acid, treating the solution of nitrosulfonic acid thus formed with vapors of HNO_3 , thus forming concentrated nitric acid and strong nitrous gases, absorbing the

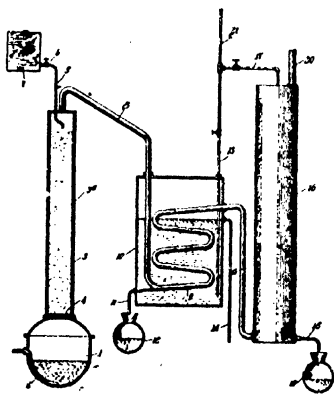


FIG. 86.—JENSEN NITRIC ACID CONCENTRATION PLANT

latter in water and using the dilute acid thus produced for treating the nitrosulfonic acid obtained by absorbing with nitrous gases in concentrated sulfuric acid. He has devised an apparatus for carrying out his process (Fig. 86).

The F. Zeisberg nitric acid concentration apparatus¹ comprises a still filled with 80% sulfuric acid and heated until the acid boils vigorously. A mixture of HNO_3 and H_2SO_4 is fed from a tank and allowed to flow down into a column filled with pumice stone. Strong nitric acid vapor passes out through a pipe and is condensed in the coil and drawn off at a suitable point. The small amount of lower nitrogen oxides formed by decomposition are absorbed by water in a separate tower. The temperature in the still is maintained around 200° and at the top of the column about 86° , a mixture of 50% nitric acid and 90% sulfuric acid in the proportion of one to three being fed into the retort from an elevated tank.

In concentrating nitric acid in a countercurrent with sulfuric acid as devised by the Norsk. Hydro-Elektrisk Kvaestofaktieselskab and E. Collet,² the requisite temperature is main-

1. U. S. P. 1197167, 1916; abst. C. A. 1916, **10**, 2966; J. S. C. I. 1916, **35**, 1058. Can. P. 178118, 1917; abst. C. A. 1918, **12**, 83. In a more recent process as described by F. Zeisberg (U. S. P. 1292948, 1919; abst. J. S. C. I. 1919, **38**, 285-A) a mixture containing not less than 64% sulfuric acid and from 3% 25% nitric acid is injected into a concentrating tower through a distributor having a number of openings with a uniform discharge, and is subjected therein to the action of a hot gaseous current. Nitric acid vapors are removed from the tower and condensed. See B. Thomas, U. S. P. 1283598, 1919; abst. J. S. C. I. 1919, **38**, 73-A. J. Hunter, New Zeal. P. 34032, 1913. W. Russell, U. S. P. 1315241; abst. C. A. 1919, **13**, 2785, has described a tank suitable for holding concentrated nitric acid. H. Kirchhofer, D. R. P. 262464, 1912; abst. J. S. C. I. 1913, **32**, 909.

2. E. P. 27239, 1913; abst. C. A. 1915, **9**, 1375. E. P. 19792, 1914; abst.

tained in the concentrating tower by introducing the nitric acid, as a mixture of liquid vapor, preferably produced by boiling the nitric acid outside the tower.

Colin¹ prepares fuming nitric acid up to a sp. gr. of 1.5, by distilling nitric of 1.4 gravity with sulfuric acid (1.84) in cast iron enamel retorts, employing a 3-way glass stopcock for separating the fractions.

The H. Frasch method for the preparation of highly concentrated nitric acid² embraces the passing of vapors from the nitric acid retort through a tower heated above the boiling point of the acid operated upon, and in which concentrated sulfuric acid or other dehydrating substance, is allowed to trickle down, anhydrous sodium sulfate or burnt plaster of Paris being claimed as efficient in this connection.

This process is somewhat similar to that of A. Erourard,³ who fortifies dilute nitric acid or the waste acids from nitrating processes by the addition of strong sulfuric acid or other body having a powerful avidity for water, such as calcium chloride, subsequently distilling the mixture in a vessel constructed in such a

J. S. C. I. 1915, **34**, 1053. D. R. P. 278867, 1913; abst. C. A. 1915, **9**, 1101; Chem. Zentr. 1914, **85**, II, 1079; Chem. Ztg. Rep. 1914, **38**, 522; Wag. Jahr. 1914, **60**, I, 357; Zts. ang. Chem. 1914, **27**, 622. D. R. P. 289745, 1914; abst. C. A. 1916, **10**, 2620; Chem. Zentr. 1916, **87**, I, 238; II, 113; Chem. Ztg. Rep. 1916, **40**, 64; Zts. ang. Chem. 1916, **29**, 89. D. R. P. 292385; abst. C. A. 1917, **11**, 1525; Chem. Ztg. Rep. 1916, **40**, 239; Zts. ang. Chem. 1916, **29**, 352. D. R. P. 305915; abst. Chem. Zentr. 1918, **89**, II, 236. F. P. 464909, abst. C. A. 1914, **8**, 3356; Mon. Sci. 1916, **83**, 12; Chem. Ztg. Rep. 1914, **38**, 479. 463859, 1913; abst. C. A. 1914, **8**, 2927; Chem. Ztg. Rep. C. A. 1914, **38**, 310. Aust. P. 71146, 1916; abst. C. A. 1916, **10**, 2505. Swiss P. 55930, 1911; 67430, 1913; 72824, 1916; 74526, 74715, 1917. Swiss P. 73573, 1916; abst. C. A. 1917, **11**, 872. Swed. P. 41509, 1916; abst. C. A. 1917, **11**, 526. U. S. P. 1031865, 1912; abst. C. A. 1912, **6**, 2676. U. S. P. 854928, 1907; abst. Chem. Ztg. Rep. 1907, **31**, 371; Mon. Sci. 1907, **67**, 153. U. S. P. 1079541, 1913; abst. C. A. 1914, **8**, 405; Mon. Sci. 1914, **81**, 27. U. S. P. 1133840, 1154289, 1158181, 1915; 1194926, 1916; abst. J. S. C. I. 1916, **35**, 966. U. S. P. 1197167, 1916; abst. J. S. C. I. 1916, **35**, 1058. F. P. 120378, 124191; abst. J. S. C. I. 1919, **38**, 817 A; C. A. 1919, **13**, 640. See also, Norske Aktieselskab. f. Elektrokemisk Ind. and B. Halvorsen, E. P. 3680, 1906; abst. J. S. C. I. 1906, **25**, 1146; F. P. 363157, 1906; abst. J. S. C. I. 1906, **25**, 847; Mon. Sci. 1907, **69**, 92.

1. F. P. 211045; abst. Mon. Sci. 1891, **37**, 892.

2. U. S. P. 517098, 1894. D. R. P. 82578; abst. Wag. Jahr. 1895, **41**, 100.

3. D. R. P. 62714; abst. Ber. 1892, **25**, 696; Wag. Jahr. 1892, **38**, 356; Zts. ang. Chem. 1892, **5**, 435. For details of the B. Thomas method of concentrating nitric acid, see U. S. P. 1283598, 1918; abst. C. A. 1919, **13**, 166. C. McCodr, Can. P. 187662, 1918; abst. C. A. 1919, **13**, 168.

manner that the vapors are caused to travel in a zig-zag direction.

The concentration process of C. Uebel¹ is best accomplished in stages, the dilute nitric acid being distilled, first at higher temperatures with sulfuric acid of medium concentration, the distillate being then brought in contact with more concentrated vitriol. From this second treatment the nitric acid is obtained in 70% to 75% concentration, and is rendered still further anhydrous by re-distillation where a vapor of 90% to 92% results. This, by partial cooling, can be made to yield a large fraction of 95% to 98% absolute HNO₃. It is claimed also that the waste acid from nitrating processes may be economically utilized by this method. According to the processes of the Swedish Nitric Syndicate,² weak nitric acid, preferably that obtained by the oxidation of atmospheric nitrogen, may be advantageously concentrated by distilling with sulfuric acid in a continuous manner, the acids flowing down an externally heated column where they meet a current of hot air passing upwards in the same column. Or, concentration may be advantageously effected in two stages, in the first of which about 60% strength is obtained by direct

1. D. R. P. 210803; abst. Mon. Sci. 1912, **77**, 99; Chem. Zentr. 1909, **80**, II, 159; Chem. Ztg. Rep. 1909, **33**, 339; Chem. Zts. 1910, **9**, No. 1565; Jahr. Chem. 1909, **62**, 536; Wag. Jahr 1909, **55**, I, 418; Zts. ang. Chem. 1909, **22**, 1468; Zts. Schiess. Spreng. 1909, **4**, 291. Compare also: D. Montiehl, U. S. P. 1271349, 1918; abst. C. A. 1918, **12**, 1848; E. Bergve, U. S. P. 1273991, 1918; abst. C. A. 1918, **12**, 2045; H. Pauling, U. S. P. 1074287, 1913; abst. J. S. C. I. 1913, **32**, 1009; Bagley, E. P. Appl. 4796, 1918; abst. J. S. C. I. 1918, **37**, 195-A; E. Maxted and T. Smith, E. P. Appl. 4906, 1917; abst. J. S. C. I. 1917, **36**, 40; Meister, Lucius & Bruening, E. P. 13842, 1914; D. R. P. Appl. June 21, 1913; abst. J. S. C. I. 1914, **33**, XV; Command-Gesellschaft für den Bau von Feueringsverd., addn. to F. P. 311776, 1901; abst. J. S. C. I. 1903, **22**, 297; Norsk. Hydro Elektrisk Kvaestofaktieselskab, D. R. P. 305915, 1915, addn. to D. R. P. 278867; F. P. 465504, 1913; abst. J. S. C. I. 1914, **33**, 466-A, 643; T. Oliver, U. S. P. 1195075, 1916; abst. J. S. C. I. 1916, **35**, 1015; E. Bergve, U. S. P. 1273991, 1918; abst. J. S. C. I. 1918, **37**, 622-A; Norsk. Hydro-Elektrisk Kvaestofaktieselskab, E. P. 116495, 1918; abst. C. A. 1918, **37**, 2113; H. Schefflein, F. P. 451515, 1912; abst. J. S. C. I. 1913, **32**, 601.

2. E. P. 6265, 1908; abst. J. S. C. I. 1908, **27**, 501. E. P. 10591, 10592, 1909; abst. C. A. 1911, **5**, 162; J. S. C. I. 1910, **29**, 88, 212. F. P. 350619, 350620, 402078, 402079; abst. J. S. C. I. 1909, **28**, 1197; J. Soc. Dyers Col. 1905, **21**, 182; Mon. Sci. 1906, **65**, 101; Chem. Ztg. 1905, **29**, 749. Swiss P. 48703, 1909. D. R. P. 170585; abst. Zts. ang. Chem. 1907, **20**, 324. 179825; abst. Zts. ang. Chem. 1907, **20**, 1327. D. R. P. 188231, 1904; abst. Zts. ang. Chem. 1908, **21**, 558. D. R. P. 233031, 236341; abst. Zts. ang. Chem. 1911, **24**, 1580; Chem. Zentr. 1911, II, 214; C. A. 1911, **5**, 3612. Aust. P. 43740, 1910; 50652. See also P. Sohlman and C. Lundholm, U. S. P. 1009197, 1911; abst. C. A. 1912, **6**, 277; J. Soc. Dyers Col. 1912, **28**, 43. T. Sohlman and W. Wilson, U. S. P. 1009196, 1911; abst. C. A. 1912, **6**, 277; Mon. Sci. 1912, **77**, 130.

contact with the gases from an electric furnace; and in the second or final phase, 90% to 93% absolute nitric acid is obtainable by distilling the strong sulfuric acid as above mentioned. The waste heat from the furnace gases is ingeniously utilized.

The essence of the invention of O. Dieffenbach¹ resides in the fact that, in concentrating dilute nitric acid, the heretofore used concentrated sulfuric acid is substituted by alkaline polysulfates, as NaHSO_4 , H_2SO_4 , or $\text{Na}_2\text{S}_2\text{O}_7 \cdot \text{H}_2\text{SO}_4$, claim being based on the fact that these bodies do not decompose when concentrated as is the case with sulfuric acid. In an example cited, if 100 grams of nitric acid of 36° Bé. are heated with one kilo of polysulfate of the composition of $\text{NaHSO}_4 \cdot \text{H}_2\text{SO}_4$, to 105° to 120°, the major portion of nitric acid distills off as 95% HNO_3 , the remaining polysulfate being readily recovered and concentrated. This is similar to the process of the Chemische Fabrik Griesheim-Electron,² in which the dilute nitric acid at 110° to 130° is mixed with polysulfate, the concentrated acid being then distilled off and the temperature raised to 250° to 300° in order to dehydrate the polysulfates for economical re use.

E. Brauer³ has patented the use of phosphoric or arsenic acid, alone or mixed, as a hygroscopic body for the removal of water from dilute nitric acid.

O. Dieffenbach and C. Uebel⁴ prefer pyro- or meta-phosphoric acids or the analogous arsenic acids or acid salts of these in vessels made of quartz, they having found that upon heating aqueous nitric acid to 110°-115° with pyro-phosphoric acid a nitric acid of 99% strength is obtainable. The ortho-phosphoric

1. D. R. P. 174736, 1903; abst. C. A. 1907, **1**, 805; Mon. Sci. 1909, **69**, 153; Chem. Centr. 1906, **77**, II, 1091; Chem. Ztg. Rep. 1906, **30**, 325; Chem. Zts. 1907, **6**, 19; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1906, **52**, I, 446; Zts. ang. Chem. 1907, **20**, 973; Zts. Schiess. Spreng. 1906, **1**, 343. F. P. 371688. Aust. P. 28968, 1907.
2. U. S. P. 819262; abst. Chem. Zts. 1906, **5**, 303; Mon. Sci. 1907, **67**, 12. F. P. 358373; abst. Mon. Sci. 1906, **65**, 128; Chem. Ztg. 1906, **30**, 224. E. P. 19986, 1905; abst. J. S. C. I. 1906, **25**, 696.
3. U. S. P. 1008690, 1911; abst. C. A. 1912, **6**, 277. E. P. 14381, 1910; abst. C. A. 1911, **5**, 2920; J. S. C. I. 1911, **30**, 27. Aust. P. 47105, 1910. F. P. 417166, 1910; abst. Mon. Sci. 1913, **79**, 83. D. R. P. 222680; abst. Mon. Sci. 1914, **81**, 77; Chem. Zentr. 1910, **81**, II, 253; Chem. Ztg. Rep. 1910, **34**, 297; Jahr. Chem. 1910, **63**, I, 587; Wag. Jahr. 1910, **56**, I, 484; Zts. ang. Chem. 1910, **23**, 1385; Zts. Schiess. Spreng. 1910, **5**, 257. Aust. P. 47105.
4. D. R. P. 238370, 1909; abst. C. A. 1912, **6**, 1663; Chem. Zentr. 1911, **82**, II, 1078; Chem. Ztg. Rep. 1911, **35**, 503; Wag. Jahr. 1911, **57**, I, 470; Zts. ang. Chem. 1911, **24**, 2029; Zts. Schiess. Spreng. 1911, **6**, 411.

acid remaining is re-treated into pyro-phosphoric acid by heating to 210°-235°. In the distillation of nitric acid, according to the process of F. Beers, a still is heated by hot oil which is circulated through a jacket around the still, the atmosphere of the still being regulated by varying both the quantity and the temperature of the oil brought into contact with the still.¹ In another process,² highly concentrated nitric acid is obtained by utilization of the heat of the nitrogen oxide-containing gases coming from the electric furnace, the dilute nitric acid being first concentrated to the fullest extent possible by direct contact with the hot gases, the product being then highly concentrated by distillation with strong sulfuric acid.

D. Collet³ employs hot water as the means to concentrate nitric acid, the escaping gases and vapors being passed through a column fed with dilute nitric acid, then through a cooling member and finally into and through a vessel filled with lumps of quicklime. It is claimed that 60% nitric acid may be obtained by this method, and more economically than by any other method heretofore disclosed.

O. Boeters and R. Wolfenstein⁴ heat ordinary nitric acid of 65% to 70% in an iron retort to which is connected a series of stoneware receivers kept at about 100° by water-, oil- or sand-

1. U. S. P. 1140351, 1915; abst. C. A. 1915, **9**, 1832; Chem. Ztg. Rep. 1916, **40**, 132.

2. Aktiebol. Swedish Nitric Syndikate, D. R. P. 233031, 1909; abst. C. A. 1911, **5**, 2710; Chem. Zentr. 1911, **82**, I, 1261; Chem. Ztg. Rep. 1911, **35**, 229; Wag. Jahr. 1911, **57**, I, 168; Zts. ang. Chem. 1911, **24**, 856; Zts. Schiess. Spreng. 1911, **6**, 156. D. R. P. 236341, 1909; abst. C. A. 1911, **5**, 3613; Chem. Zentr. 1911, **82**, II, 314; Chem. Ztg. Rep. 1911, **35**, 392; Wag. Jahr. 1911, **57**, I, 469; Zts. ang. Chem. 1911, **24**, 1580. Aust. P. 43740, 1910.

3. U. S. P. 854928, 1003433; abst. J. S. C. I. 1910, **29**, 1010; 1079541, 1133840, 1915; abst. C. A. 1915, **9**, 1374. See also C. A. 1915, **9**, 516, 1138400, 1158181, 1915; abst. C. A. 1915, **9**, 3336. 1184926, 1916; abst. C. A. 1916, **10**, 1916. E. P. 26098, 1912; 7597, 1913; abst. C. A. 1914, **8**, 3102. E. P. 22746, 1913; abst. C. A. 1915, **9**, 850. F. P. 357221; abst. C. A. 1907, **1**, 477; Mon. Sci. 1906, **65**, 126. F. P. 412768, 447106, 1912; abst. C. A. 1913, **7**, 2457; Mon. Sci. 1913, **79**, 76; Chem. Ztg. Rep. 1913, **37**, 180. F. P. 450448; abst. C. A. 1913, **7**, 2999; Chem. Ztg. Rep. 1913, **37**, 281. Aust. P. 62169. Can. P. 157489, 157490. Nor. P. 13925; abst. Chem. Ztg. 1905 **29**, 457; Mon. Sci. 1905, **63**, 116.

4. D. R. P. 189865; abst. Mon. Sci. 1910, **73**, 66; Chem. Zentr. 1907, **78**, II, 1954; Chem. Zts. 1907, **6**, No. 424; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1907, **53**, I, 409; Zts. ang. Chem. 1908, **21**, 798; Zts. Schiess. Spreng. 1907, **2**, 410. D. R. P. 191912; abst. Mon. Sci. 1910, **73**, 67; Chem. Zentr. 1908, **79**, I, 315; Chem. Ztg. Rep. 1907, **31**, 633; Chem. Zts. 1908, **7**, 490; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1907, **53**, I, 410; Zts. ang. Chem. 1908, **21**, 798; Zts. Schiess. Spreng. 1907, **2**, 435.

bath, these being charged with a dehydrated nitrate. When this has absorbed sufficient water, that particular receiver is disconnected from the series by means of a 3-way tube and is connected with a vacuum whereby the nitrate is dehydrated and purified for re-use. As a specific nitrate for dehydration,¹ these inventors specify calcium nitrate dehydrated at 150° to 200°, by which treatment it assumes a highly porous character.

For the concentration of nitric acid up to 63% strength, from 1.25 to 1.5 parts of calcium nitrate is said to be required.

The Farbwerke vorm. Meister, Lucius and Brüning² dissolve gases of liquid nitrogen peroxide in commercial nitric acid of 60% to 62% strength, treating this mixture with oxygen whereby the peroxide is oxidized to nitric acid, and concentrated acid thereby obtained.

The process of the Salpetersäure Industrie Gesellschaft is analogous.³

The improvement in nitric acid concentration processes as devised by H. Pauling⁴ is characterized, first, by electrolyzing aqueous nitric acid, liquefying the nitric oxides generated at the cathode, and passing the product into the acid surrounding the anode; and secondly, by filling the anode leg of the U-tube adapted for electrolysis with sulfuric acid, and the cathode leg with dilute nitric acid, this liquid then being electrolyzed.

The Salpetersäure Industrie Gesellschaft⁵ have called atten-

1. U. S. P. 864217, 1907; abst. Mon. Sci. 1908, **69**, 49. E. P. 28449, 1906; abst. C. A. 1907, **1**, 2522; J. S. C. I. 1907, **26**, 760. F. P. 374797; abst. Mon. Sci. 1908, **69**, 81; Chem. Ztg. Rep. 1907, **31**, 175, 183; 1908, **32**, 245. D. R. P. 62714; abst. Ber. 1892, **25**, 696; Wag. Jahr. 1892, **38**, 356; Zts. ang. Chem. 1892, **5**, 435.

2. E. P. 15948, 1911; abst. J. S. C. I. 1911, **30**, 930; 1912, **31**, 775. C. A. 1913, **7**, 223. F. P. 432990, 1911; abst. J. S. C. I. 1912, **31**, 127; C. A. 1912, **6**, 2502; Mon. Sci. 1913, **79**, 130; Chem. Ztg. Rep. 1912, **36**, 105.

3. F. P. 368716, 1906; abst. J. S. C. I. 1907, **26**, 24. D. R. P. 249328; abst. C. A. 1912, **6**, 2984; Chem. Zentr. 1912, **83**, II, 464; Chem. Ztg. Rep. 1912, **36**, 462; Wag. Jahr. 1912, **58**, I, 416; Zts. ang. Chem. 1912, **25**, 1649. For the manufacture of highly concentrated nitric acid according to the Chemische Fabrik Rhenania, see E. P. 27240, 1898; D. R. P. 106962; abst. Mon. Sci. 1900, **56**, 117; Chem. Centr. 1900, **71**, I, 636; Chem. Ztg. 1900, **24**, 80; Chem. Zts. 1902, **1**, 14; Jahr. Chem. 1900, **53**, 239; Wag. Jahr. 1899, **45**, 407; Zts. ang. Chem. 1899, **12**, 1138. Swiss P. 24001, 1901.

4. E. P. 18603, 1906; abst. C. A. 1907, **1**, 1171, 1194; J. S. C. I. 1907, **26**, 157. For the continuous process of nitric acid distillation of M. Prentic, see E. P. 6960, 1893; U. S. P. 526116, 1893; D. R. P. 79645; abst. Ber. 1895, **28**, 482; Jahr. Chem. 1895, **48**, 569; Wag. Jahr. 1895, **41**, 450; Zts. ang. Chem. 1895, **8**, 170.

5. E. P. 18113, 1913; 23385, 1908; abst. J. S. C. I. 1910, **29**, 88; 1914, **33**, 790. D. R. P. 180052, 1905; abst. C. A. 1907, **1**, 1936; Mon. Sci. 1909, **71**,

tion to the fact that in concentrating dilute nitric acid by distilling in the presence of sulfuric acid or other hygroscopic agent with the aid of a countercurrent of steam or a mixture of gas and steam, a portion of the concentrated acid obtained as distillate is returned to the mixture under treatment. By this means a less concentrated vitriol than that usually employed may be used as the desiccant. The nitric acid thus returned is preferably the relatively weak acid obtained in the first of the series of condensers. The process is claimed to be especially applicable to the recovery of the waste acids obtained in the manufacture of nitroglycerol.

The Verein Chemische Fabriken in Mannheim¹ interpose between the still and the condensing units a dephlegmator from which the dilute acid runs back into the still as it condenses. The atmosphere of the dephlegmator is maintained in the neighborhood of 85° in order that the concentrated acid may pass on to the condensing apparatus. Nitric acid of 60%-62% is concentrated to a higher point by the Farbwerke Höchst, vorm. Meister, Lucius & Brüning,² by passing a mixture of nitrogen peroxide and oxygen through it. Compressed oxygen may also be employed,³ the escaping nitric oxide and oxygen gases being

74; Chem. Zentr. 1907, **78**, I, 1083; Chem. Ztg. Rep. 1907, **31**, 86; Jahr. Chem. 1905-1908, I, 1794; Wag. Jahr. 1906, **52**, I, 446; Zts. ang. Chem. 1907, **20**, 1329; Zts. Schiess. Spreng. 1907, **2**, 35. D. R. P. 211919, 1907; abst. C. A. 1910, **4**, 238; Mon. Sci. 1912, **77**, 99; Chem. Zentr. 1909, **80**, II, 944; Chem. Ztg. Rep. 1909, **33**, 420; Jahr. Chem. 1909, **62**, I, 373; Wag. Jahr. 1909, **55**, I, 604; Zts. ang. Chem. 1909, **22**, 1724. F. P. 374237, 1907; 407133, 1910; abst. Mon. Sci. 1908, **69**, 139; 1910, **73**, 175; Chem. Ztg. Rep. 1907, **31**, 309; 1909, **33**, 299; 1910, **34**, 187. Aust. P. 61387.

1. D. R. P. 85042; abst. Ber. 1896, **29**, 245; Chem. Ztg. 1896, **20**, 193; Wag. Jahr. 1896, **42**, 408; Zts. ang. Chem. 1896, **9**, 139. D. R. P. 281211, 1914; abst. Chem. Zentr. 1915, **86**, I, 229; Chem. Ztg. Rep. 1915, **39**, 31; Zts. ang. Chem. 1915, **28**, 82. E. P. 20189, 1912. F. P. 462290, 1914; abst. C. A. 1914, **8**, 2464; Chem. Ztg. Rep. 1914, **38**, 230. Hausmann, U. S. P. 1115192; abst. C. A. 1915, **9**, 129; Mon. Sci. 1915 **82**, 18.

2. F. P. 432990, 1911; abst. C. A. 1912, **6**, 2502; J. S. C. I. 1912, **31**, 127; Mon. Sci. 1913, **79**, 130; Chem. Ztg. Rep. 1912, **36**, 105.

3. Farbwerke vorm. Meister Lucius u. Brüning, E. P. 15948, 1911; abst. C. A. 1913, **7**, 223; J. S. C. I. 1911, **30**, 930; 1912, **31**, 775. E. P. 13842, 1913; abst. C. A. 1915, **9**, 3337. E. P. 4345, 1915; abst. C. A. 1916, **10**, 2281; J. S. C. I. 1916, **35**, 537. F. P. 433502, 453845 addn. dated April 17, 1914, to E. P. 453845, 473775; abst. J. S. C. I. 1914, **33**, 483; 1915, **34**, 491, 552. C. A. 1913, **7**, 3645; Chem. Ztg. Rep. 1913, **37**, 474; U. S. P. 1253534, 1918; abst. J. S. C. I. 1918, **37**, A, 150. D. R. P. 220539, 249328, 249329, 286751, 1910; abst. C. A. 1912, **6**, 2984; 1916, **10**, 1412; Mon. Sci. 1914, **81**, 76; Chem. Zentr. 1910, **81**, I, 1397; 1912, **83**, II, 464; 1917, **88**, I, 638; Chem. Ztg. Rep. 1910, **34**, 179; 1912, **36**, 445, 462; 1915, **39**, 357;

gradually re-introduced into the process in small amounts.

The Societe Le Nitrogene¹ manufacture concentrated nitric acid from N_2O_4 by treating a molecular mixture of the N_2O_4 and water with oxygen under pressure. They also claim that wood charcoal saturated with peroxide may be advantageously employed.

In order to avoid the use of expensive vessels for distilling crude nitric acid, as those of porcelain or platinum, J. Waldbauer² fills the stills partially full of such granular material as sand, pebbles, broken glass, or other form of silica, preferably insulating the sides of the vessel by placing fine sand, followed by a layer of coarser sand toward the center and larger pebbles in the middle. The acid is run into this still and is intended to be evaporated before it reaches the walls of the still. This process if, successful, admits of the employment of stills made of cheap and durable materials which would be unsuitable if the acid came in direct contact with it.

C. Schlarb³ takes nitrous gases from any source, treats them with water in the presence of iron, aluminium or chromium oxides or basic nitrates, subsequently driving off the nitric acid from the nitrate liquors obtained by continuous heating under diminished pressure.

In the Vietinghoff-Scheel process⁴ the acid is concentrated

Chem. Zts. 1910, **9**, No. 1876; Jahr. Chem. 1910, **63**, 1, 588; Wag. Jahr. 1910, **56**, 1, 480; 1912, **58**, 1, 416, 447; Zts. ang. Chem. 1910, **23**, 1050; 1912, **25**, 1649; Zts. Schiess. Spreng. 1910, **5**, 175, 1912, **7**, 418; D. R. P. 289562, Addn. to 286751; abst. Chem. Zentr. 1916, **87**, 1, 192, Chem. Ztg. Rep. 1916, **40**, 48; Zts. ang. Chem. 1916, **29**, 69, abst. C. A. 1916, **10**, 2620. Norw. P. 27064, 1916; abst. C. A. 1916, **10**, 2787. Swed. P. 34895, 40600, 41751, 1916; abst. C. A. 1917, **11**, 1269. Swiss P. 56595, 57050, 69177, 71189. Aust. P. Appl. 7082, 1915. Aust. P. 55242, 55243, 55244, Neth. P. 764; abst. Chem. Ztg. Rep. 1913, **37**, 345; C. A. 1913, **7**, 3252. U. S. P. (M. Moest, R. v. Berneck and J. Opl.) 1050160 (M. Moest and M. Eckardt), 1145162, 1915, abst. C. A. 1913, **7**, 871; 1915, **9**, 1015, 2432. F. Foerster and M. Koch, Zts. ang. Chem. 1908, **21**, 2168.

1. E. P. 1143, 1911; abst. Chem. Ztg. Rep. 1912, **36**, 371. F. P. 424598, 1911; abst. C. A. 1912, **6**, 1969. Mon. Sci. 1913, **79**, 118; Chem. Ztg. Rep. 1911, **35**, 303. Aust. P. Appl. A 133; Aust. P. 53148, 1911. See also J. Leitch, E. P. Appl. 12914, 1916; abst. J. S. C. I. 1916, **35**, 57.

2. D. R. P. 155006; abst. Mon. Sci. 1905, **63**, 51; Chem. Centr. 1904, **74**, II, 1267; Chem. Ztg. 1904, **28**, 1001; Chem. Zts. 1905, **4**, 123; Jahr. Chem. 1904, **57**, 490; Wag. Jahr. 1904, **50**, 1, 338; Zts. ang. Chem. 1905, **18**, 105.

3. D. R. P. 243840; abst. C. A. 1912, **6**, 2299; Chem. Zentr. 1912, **83**, I, 865; Chem. Ztg. Rep. 1912, **36**, 156; Wag. Jahr. 1912, **58**, 1, 417; Zts. ang. Chem. 1912, **25**, 596; Zts. Schiess. Spreng. 1912, **7**, 185. Aust. P. 51926, 1911.

4. D. R. P. Appl. V-8284.

by first converting into ammonium nitrate which is dried and distilled with strong sulfuric acid.

The mechanical arrangement devised by G. Plath¹ for the production of a colorless and concentrated nitric acid comprizes interposing a cooling worm about 80 feet long between perpendicular cooling pipes and the receiver, air being forced through in the direction contrary to the current of acid, the temperature of the chamber being regulated in such a manner that the cooled fraction is obtained substantially free from the lower nitrogen oxides.

F. Hale and A. Scott² absorb the dilute nitric acid in kieselguhr or other diatomaceous material, afterwards heating this under reduced pressure in an earthenware or cast-iron retort. By adjusting the temperature and speed of distillation and the absoluteness of vacuum, a wide range in concentration of nitric acid may be effected.

In the F. Nathan and J. and W. Thomson process which has been widely used,³ nitric acid vapors are passed from the bottom upwards through cooling worms which, in turn, are immersed in running water to the top of the coil. The upper ends of the worms being connected with a vacuum, nitric acid issuing at the bottom is substantially free of lower nitrogen oxides.

W. Hof⁴ and G. Krell⁵ and the Sprengstoff Akt.-Ges. Carbonit⁶ have also obtained patent protection for the distillation and concentration of nitric acid.

T. Raschig⁷ distils nitric acid with concentrated sulfuric

1. E. P. 9133, 1901; abst. J. S. C. I. 1902, **21**, 772.
2. E. P. 24379, 1910; abst. C. A. 1912, **6**, 1504; J. S. C. I. 1911, **30**, 1251; Chem. Ztg. Rep. 1912, **36**, 170. E. P. 25386, 1910; abst. C. A. 1912, **6**, 1505; J. S. C. I. 1911, **30**, 1251; Chem. Ztg. Rep. 1912, **36**, 194.
3. F. P. 406806; abst. Chem. Ztg. Rep. 1910, **34**, 151.
4. D. R. P. 279131, 1912; abst. C. A. 1915, **9**, 1231; Chem. Zentr. 1914, **85**, II, 1078; Chem. Ztg. Rep. 1914, **38**, 557; Wag. Jahr. 1914, **60**, I, 568; Zts. ang. Chem. 1914, **27**, 617. E. P. 463208; abst. C. A. 1914, **8**, 2607; Chem. Ztg. Rep. 1914, **38**, 250.
5. E. P. 4063, 1907; abst. C. A. 1907, **1**, 630, 658.
6. E. P. 11854, 1913; abst. C. A. 1914, **8**, 2807; J. S. C. I. 1913, **32**, 1130; Chem. Ztg. Rep. 1914, **38**, 290.
7. D. R. P. 286122; abst. Chem. Ztg. Rep. 1915, **39**, 306; Zts. ang. Chem. 1915, **28**, 441. D. R. P. 286973, 1914; abst. J. S. C. I. 1916, **25**, 114; Chem. Zentr. 1917, **88**, I, 729; Chem. Ztg. Rep. 1915, **39**, 387; Zts. ang. Chem. 1915, **28**, 522. D. R. P. 292622; abst. J. S. C. I. 1916, **35**, 916; Chem. Ztg. Rep. 1916, **40**, 237; Zts. ang. Chem. 1916, **29**, 368. U. S. P. 1130104, 1163174; abst. J. S. C. I. 1916, **35**, 116. E. P. 3208, 1915; abst. J. S. C. I. 1915, **34**, 962. F. Nathan and J. and W. Thomson, F. P. 406806; abst. Chem. Ztg. Rep. 1910, **34**, 151.

acid at atmospheric pressure, the dilute sulfuric acid remaining being fed continuously and automatically through a bent barometer tube into a heated vacuum pan situated above, its ascent being assisted by the introduction of air bubbles into the barometer tube, when concentrated sulfuric acid is passed back by gravity down a similar tube into the first pan. Spent nitrating acid may be resolved in this way into water, nitric acid and sulfuric acid, the last named being removed from circulation without interrupting the process. Any nitrosulfonic acid formed in the process is converted into nitric and sulfuric acids by introducing hydrogen peroxide or Caro's acid with nitric acid.

The method of M. Moest¹ for preparing highly concentrated nitric acid involves mixing the nitric acid with a larger proportion of liquid NO_2 than corresponds with the maximum solubility, and claims that if this mixture is left at rest two thin separate layers are rapidly formed. The observation has been made that each of these homogeneous layers again consists of nitric acid and nitrogen peroxide, and that one of these layers—usually that of the lower specific gravity—contains a more concentrated acid—under favorable conditions, nitric acid of about 100% strength. It thus becomes possible to separate the nitric acid and water from aqueous nitric acid by introducing nitrogen peroxide.

L. Friderich² prepares highly concentrated nitric acid by treating a mixture of equal molecular proportions of nitric peroxide and water with oxygen under pressure. The process is carried out in an autoclave provided with a stirring apparatus.

1. E. P. 1345, 1915; U. S. P. 1180651; Swed. P. 40600; abst. J. S. C. I. 1916, **35**, 537, 635; Chem. Ztg. Rep. 1917, **41**, 124. See Verein Chemische Fabriken, E. P. 20189, 1913; abst. J. S. C. I. 1914, **33**, 485. With the B. Dawson (E. P. 120869, 1918; J. S. C. I. 1919, **38**, 73) apparatus, in the absorption of nitrous gases by projecting sprays of water or weak acid from the bottom of an unobstructed tower by means of air jets, each jet is provided with a funnel shaped attachment. The wide end of the funnel projects above the level of the liquid in the tower, while the apex surrounds, and is attached to the jet at a point some distance below the water level. Access of the liquid to the interior of the funnel is obtained by means of holes near the apex and just below the tip of the jet. By means of this device efficient spraying can be effected notwithstanding variations in the level of liquid in the tower.

2. E. P. 319, 1911; abst. C. A. 1911, **5**, 3136; J. S. C. I. 1911, **30**, 684, Chem. Ztg. Rep. 1911, **35**, 392. According to P. Guye (E. P. 131335, 1918; J. S. C. I. 1919, **38**, 763-A) aqueous nitric acid is concentrated by passing into it a current of ozonized oxygen or air and nitrogen peroxide which interact to form nitric anhydride, the latter combining with the water present in the nitric acid.

liquid peroxide being first introduced and the water added in small quantities at a time while oxygen under pressure is being forced in. The I. Hechenbleikner apparatus¹ comprises a series of absorption towers arranged in a row with reservoirs at their lower ends having overflow outlets successively from one to another in a row. Pumps and piping are arranged so that liquid from each reservoir can be pumped to the top of its own tower for recirculation. The gases flow through the towers in the same direction as the liquid.

In the method as described by J. Leitch,² a mixture of weak nitric acid or sodium nitrate and weak (80%) sulfuric acid is heated in a still and the vapor passed through a dephlegmating column the temperature of which can be registered. Distillation may be effected under vacuum or reduced pressure. Weak acid condenses in the dephlegmator and returns to the still, while the stronger acid passes over and is condensed.

O. Baither and the Chemische Fabrik Greisheim Elektron³ concentrate nitric acid by constantly blowing air through a quantity of hot sodium polysulfate (H_2NaSO_4)₂ in a still, mixing a charge of dilute nitric acid with this polysulfate and distilling concentrated nitric acid from the mixture.

The Badische Anilin & Soda Fabrik⁴ manufacture nitrates by acting on a solution of a nitrite or a solution containing both

1. U. S. P. 1314802, 1919; abst. C. A. 1919, **13**, 2742.
2. E. P. 125616, 1916; abst. J. S. C. I. 1919, **38**, 413-A; C. A. 1919, **13**, 2258.
3. F. P. 358373, 1905, 380884; abst. J. S. C. I. 1906, **25**, 218; 1908, **27**, 22; abst. Mon. Sci. 1906, **65**, 128; Chem. Ztg. 1906, **30**, 224. U. S. P. 819262, 1906; 971149; abst. J. S. C. I. 1906, **25**, 536; Mon. Sci. 1907, **67**, 12; 1913, **79**, 100; Chem. Ztg. Rep. 1910, **34**, 610; Chem. Zts. 1906, **5**, 303. E. P. 891, 1891; 19086, 1905; 1395, 1907; abst. J. S. C. I. 1906, **25**, 696; J. Soc. Dyers Col. 1891, **7**, 31. D. R. P. 170532, 218779; abst. C. A. 1910, **4**, 2032; Mon. Sci. 1907, **67**, 145; 1913, **79**, 158; Chem. Centr. 1906, **77**, 11, 185; 1910, **81**, 875; Chem. Ztg. 1906, **30**, 562; Chem. Ztg. Rep. 1910, **34**, 125; Chem. Zts. 1907, **6**, 19; Jahr. Chem. 1905-1908, I, 1793; 1910, **63**, I, 416; Wag. Jahr. 1906, **52**, I, 445; Zts. ang. Chem. 1906, **19**, 972; Zts. Schiess. Spreng. 1906, **1**, 180. Aust. P. 26684, 1906.
4. E. P. 30502, 1909; abst. C. A. 1911, **5**, 2918; J. S. C. I. 1910, **29**, 1455. D. R. P. 62714; abst. Ber. 1892, **25**, 696; Wag. Jahr. 1892, **38**, 356; Zts. ang. Chem. 1892, **5**, 435. D. R. P. 82573; abst. Mon. Sci. 1895, **48**, 72; 1902, **58**, 23; Ber. 1895, **28**, 876; Chem. Centr. 1895, **66**, II, 1024; Jahr. Chem. 1895, **48**, 570; Wag. Jahr. 1895, **41**, 449; Zts. ang. Chem. 1895, **8**, 570. D. R. P. 189865; abst. Mon. Sci. 1910, **73**, 66; Chem. Zentr. 1907, **78**, II, 1954; Chem. Zts. 1907, **6**, No. 424; Jahr. Chem. 1905-1908, I, 1795; Wag. Jahr. 1907, **53**, I, 409; Zts. ang. Chem. 1908, **21**, 798; Zts. Schiess. Spreng. 1907, **2**, 410. Aust. P. 34170, 1908.

nitrite and nitrate with nitric acid, causing the nitrogen oxide gases evolved to mix with oxygen, and the higher oxides of nitrogen thereby formed to be absorbed by means of water or by non-alkaline aqueous absorbents. By this means the nitric acid thus formed immediately reacts on a fresh quantity of solution containing nitrite or nitrate or both, while at the same time causing a small excess of nitric acid to participate in the reaction.

The apparatus for the purification and concentration of nitric acid as devised by W. Dieterle¹ combines with an evaporating receptacle, a condenser connected therewith comprising a series of coils, together with a vertical canal and tubes connecting the canal with a tube leading from the condenser to a receiver for the purified acid.

For the generation of solutions of nitrogen pentoxide and monohydrate nitric acid, the Elektrochemische Werke G. m. h. H.² oxidize electrolytically "nitrogen dioxide" or nitrous acid dissolved in nitric acid. For example, they assert that if 17 kilos of "nitrogen dioxide" be dissolved in 80 kilos of monohydrate nitric acid and the solution oxidized electrolytically in the anode compartment of a cell using 200 amperes per square meter at 7 volts, the nitrogen dioxide is completely oxidized by an expenditure of 11,000 ampere-hours and a concentrated acid containing 20% of dissolved nitrogen peroxide thereby obtained.

In the well-known apparatus of O. Guttmann³ for concentrating nitric acid, shown in Fig. 67 (p. 842), the advantages claimed for the apparatus are continuous working in which a constant, uniform, shallow, wide flow of liquid toward the greatest head is obtained, while at the same time provision of sufficient space above the flow of liquid for conducting the constantly arising vapor in the direction opposite to the flow of the liquid is made, as well as obtaining a uniform temperature of the vapors as they are drawn from the apparatus, the latter being of great importance

1. U. S. P. 543826, 1895.
2. E. P. 15432, 1911; abst. J. S. C. I. 1911, **30**, 1251; C. A. 1913, **7**, 27. F. P. 431006, 1911; abst. Mon. Sci. 1913, **79**, 128. D. R. P. 212423, 1909; abst. Mon. Sci. 1912, **77**, 167; Chem. Zentr. 1909, **80**, II, 569; Chem. Ztg. Rep. 1909, **33**, 439; Chem. Zts. 1910, **9**, No. 1560; Jahr. Chem. 1909, **62**, I, 535; Wag. Jahr. 1909, **55**, I, 394; Zts. ang. Chem. 1909, **22**, 1811; Zts. Schiess. Spreng. 1909, **4**, 333. Aust. P. 41946, 1909. Swiss P. 43629, 1908.
3. U. S. P. 505520, 1893.

in the concentration especially of sulfuric, as well as of nitric acid.

B. Halvorsen¹ manufactures concentrated nitric acid from nitrosulfonic and nitrous sulfuric acids by absorbing nitrous gases in sulfurous or sulfuric acid and treating with concentrated sulfuric acid with the addition, after admixture of a little water and suitable oxidizing agent of manganese dioxide, lead dioxide or chromic acid or chromates in small amounts and subsequently distilling the product for the separation of the nitric acid.

"Nitrosulfuric acid" as prepared according to the method of T. Holliday² is made by condensing nitric acid in iron vessels containing concentrated sulfuric acid, the vessels and their covers being lined with stone, tile, or other acid-resisting material.

H. Jones³ has assigned to the Armour Fertilizer Works of Chicago a method in which the acid is concentrated by allowing it to trickle down in the form of alternate pools and films, over an irregular inclined surface in an enclosed chamber while a current of hot gases passes over it. The gases are introduced at the lower part of the chamber and, by means of a baffle, directed on to the surface of the acid. The concentrated acid collects at the bottom of this chamber while the moisture-laden acids leave at the top.

The C. Kaesmacher apparatus⁴ involves a process for the separation and concentration of acids in which the liquid, in a finely divided condition, engages a current of hot air in a tower as indicated by the patentee, whereby either sulfuric acid or nitric acid of high strength is obtainable.

In contradistinction to the above, I. Moscicki⁵ places between a furnace in which the vapors of nitric acid are made from air, and the absorbing apparatus, a tower containing suitable packing, in which a mixture of 60° to 61° Bé. sulfuric acid and nitric acid is allowed to trickle down simultaneously. The furnace gases take up nitric acid from this mixture and then pass to another tower, during which passage they cool down and allow

1. U. S. P. 892516, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 423; Mon. Sci. 1909, **71**, 113. E. P. 3680, 1906; abst. C. A. 1907, **1**, 926; J. S. C. I. 1906, **25**, 1146.

2. E. P. 2193, 1882.

3. U. S. P. 1183207, 1916; abst. J. S. C. I. 1916, **35**, 736. See also J. Jouveau-Dubreuil, E. P. 56, 1879.

4. E. P. 386783, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 389.

5. D. R. P. 230170; abst. Mon. Sci. 1914, **81**, 84; Chem. Zentr. 1911, **82**, I, 357; Chem. Ztg. Rep. 1911, **35**, 66; Wag. Jahr. 1911, **57**, I, 468; Zts. ang. Chem. 1911, **24**, 281; Zts. Schiess. Spreng. 1911, **6**, 75. Aust. P. 38937.

most of the nitric acid to separate in a concentrated form. The non-condensed portion of the nitric acid is retained in the second tower, or by other suitable apparatus.

In absorbing oxides of nitrogen diluted with air and recovering the oxides as concentrated nitric acid, A. Naville and P. and O. Guye¹ cause the oxides to react with concentrated sulfuric acid containing nitrosylsulfuric acid, and then separate by distillation.

C. Rossi² intermingles nitric acid with hot air, preferably in the presence of steam, in such manner that the temperature of the gases on leaving the apparatus are kept below 100° C.; or,³ a mixture of nitric acid diluted with one and a half times its weight of concentrated sulfuric acid is forced against a current of air and steam whereby nitric acid up to 99.8% strength is alleged to be obtained. According to a variation in this process¹ nitric acid is first concentrated up to 42° Bé. in a vacuum apparatus followed by fractionation in a column apparatus.

F. Häusser⁴ produces concentrated nitric acid by first forming oxides of nitrogen by the explosion of a mixture of nitrogen, oxygen and combustible material, as benzene vapor or coal gas, the temperature produced by the explosion being carried up to 1900°-2000° if possible, this high temperature being maintained constantly as long as required for the formation of nitrogen, then suddenly chilling the gas products with cold water sufficiently to prevent the oxides formed decomposing. These chilled gases thereby utilize their potential energy and finally, after exhaustion, are passed into a cool receptacle to permit the oxides of nitrogen to further oxidize and condense to form nitric acid.

In the process of R. Schall and the Stickstoffwerke Akt.-Ges.⁶ a mixture of dilute nitric acid and a drying agent is passed

1. E. P. 6366, 1908; abst. J. S. C. I. 1908, **27**, 898. See also U. S. P. H. Rankin, F. P. 479492, 1916; abst. J. S. C. I. 1916, **35**, 1108.

2. E. P. 455531; abst. C. A. 1914, **8**, 794; Chem. Ztg. Rep. 1913, **37**, 656.

3. E. P. 455530, 455532, 463821, 1913; abst. J. S. C. I. 1914, **33**, 421; C. A. 1914, **8**, 633, 794, 3103; Mon. Sci. 1914, **81**, 11; 1916, **83**, 10; Chem. Ztg. 1913, **37**, 655, 656; 1914, **38**, 344. E. P. 23959, 1913; abst. J. S. C. I. 1914, **33**, 1154. E. P. 463825, 1913; abst. J. S. C. I. 1913, **32**, 943; 1914, **33**, 421; Mon. Sci. 1916, **83**, 10; Chem. Ztg. Rep. 1914, **38**, 344.

4. E. P. 463830; abst. C. A. 1914, **8**, 3103; Mon. Sci. 1916, **83**, 10; Chem. Ztg. Rep. 1914, **38**, 344.

5. U. S. P. 961350, 1910; abst. C. A. 1910, **4**, 2551; Mon. Sci. 1910, **73**, 130.

6. D. R. P. 280965; abst. J. S. C. I. 1915, **34**, 611; Chem. Zentr. 1915, **86**, 1, 175; Chem. Ztg. Rep. 1915, **39**, 2; Zts. ang. Chem. 1915, **28**, 82.

through a tower provided with a central tube through which flow heating gases, the mixture being compelled to flow evenly through a tower having ribs in the form of spirals or steps, this tower being conveniently made of a high silicon iron or chromium.

A compound of nitric and sulfuric anhydride has been described by W. Schultze¹ which is a solid compound of the approximate formula:



and results by heating sulfur trioxide or a gaseous mixture obtained by contact processes, in nitric acid of at least 94% concentration. A mixture of about 300 parts of fuming oil of vitriol containing 60% free sulfur trioxide and 70 parts of nitric acid of 96% strength absolute, is treated with the vapors of sulfur trioxide and nitric acid while the lower portion of the vessel is heated by means of a steam jacket to 100°. The escaping vapors of sulfur trioxide and nitric acid are passed into a lead vessel containing sulfuric acid of 97% to 98% strength, a portion of the product being allowed to run off from time to time and caused to crystallize by cooling.

In the process of the Chemical Construction Co.,² concentration may be carried on by forcing the hot gases through the acid in counter flow to agitate it and thoroughly subject it to the action of heat. The acid is subjected to an increasing temperature and agitated at the point of contact with the gas at the minimum temperature. The Tentelw Chemical Works³ describe a process for obtaining a pure nitric acid by distilling commercial nitric acid with a nitrate as zinc or nickel. The nitric acid is gradually introduced into the nitrate solution, a temperature of 126°–170° being meanwhile maintained. The rate of introduction of the crude acid is so regulated that it is about equal to the volume of the distillate, while the strength of the pure acid may be regulated by the selection of different concentrations of the nitrate solution.

The concentration of nitric or more readily sulfuric acid,

1. U. S. P. 1047576; abst. C. A. 1913, **7**, 685; Chem. Ztg. Rep. 1913, **37**, 189; Mon. Sci. 1913, **79**, 99.
2. F. P. 483881, 1917; abst. C. A. 1918, **12**, 980.
3. E. P. 110637, 1916; abst. C. A. 1918, **12**, 518; J. S. C. I. 1917, **36**, 1271.

may be accomplished, according to S. Tungay and G. Haughton,¹ by running it over the surface of a shallow inclined tray of passive iron, lead (for sulfuric acid) or fused silica, the bottom of which is corrugated transversely to increase the heating surface. A series of such trays may be arranged in cascade form, properly covered to minimize volatilization of the acid (when nitric), each tray being provided with a recessed outlet fitting within the next tray, and packed with asbestos rope.

The bulk evaporator of H. Frischer² for the manufacture of nitric acid from nitrates comprizes a retort having a number of vapor-discharge pipes connected singly or in pairs to separate coolers, and joining together toward the end of the cooling system after most of the vapor has been condensed. H. Pauling has described a process for the concentration of nitric acid which comprizes passing aqueous nitric acid in mixture with sulfuric acid or other suitable dehydrating agent against a counterflowing current of steam, or of a mixture of a large proportion of steam with gases inert toward nitric acid. The conditions of operation are so regulated that highly concentrated nitric acid vapors are obtained, while the water originally present in the nitric acid is substantially all taken up and retained by the nitric acid.³ The T. Oliver apparatus⁴ is somewhat similar. In the E. Washburn process⁵ ammonium nitrate is the product heated with sulfuric acid to produce nitric acid. The Cumming method⁶ is analogous. J. Peregrin⁷ has described the properties of "ironac" for the concentration of sulfuric acid, and "elianite" especially resistant to nitric acid, both being ferro-silicon alloys.

The methods of F. Bayer & Co.,⁸ A. Clemm,⁹ Chemical Construction Co.,¹⁰ Canadian Explosives, Ltd.,¹¹ Deutsche Gas-

1. E. P. 114072, 1917; abst. C. A. 1918, **12**, 1499; J. S. C. I. 1918, **37**, 206-A. See also E. P. 4931, 1875; 18751, 1890; 9514, 13927, 1893.
2. E. P. 7099, 1915; abst. J. S. C. I. 1916, **35**, 537.
3. U. S. P. 1031864, 1912; abst. C. A. 1912, **6**, 2676.
4. Can. P. 170811, 1916; abst. C. A. 1918, **12**, 747.
5. Can. P. 173158, 1916; abst. C. A. 1918, **12**, 205.
6. E. P. Appl. 17127, 1916; abst. J. S. C. I. 1917, **36**, 119.
7. Rev. chim. ind. 1918, **27**, 33; abst. C. A. 1918, **12**, 1497.
8. D. R. P. 310081, 1918; abst. J. S. C. I. 1920, **39**, 404-A.
9. D. R. P. 303313, 304233, 1916; abst. J. S. C. I. 1920, **39**, 294-A.
10. Can. P. 170812, 1916.
11. Can. P. 179118, 1917.

glühlicht Ges.,¹ H. Frischer,² Y. Kawakita,³ E. Maxted and T. Smith,⁴ Farbwerke vorm. Meister, Lucius & Brüning,⁵ Norsk. Hydro-Elektrisk Kvaestofaktieseskab,⁶ Societe anon. Nitrogene,⁷

1. D. R. P. 290681, 1916; abst. Chem. Ztg. 1920, **44**, 294.
2. E. P. 137834, 1920; abst. C. A. 1920, **14**, 1596.
3. Jap. P. 34872, 1919; abst. C. A. 1920, **14**, 2140.
4. E. P. 126704, 1917; abst. J. S. C. I. 1919, **38**, 499-A; C. A. 1919, **13**, 2422.
5. D. R. P. Anm. F-31526, 1910; F-32015, 1911; Aust. P. Appl. 7083, 7084, 1911; Hung. P. Appl. F-2789, 1911; Ital. P. 119060, 119494, 1911; abst. Chem. Ztg. 1912, **36**, 292, 528, 598, 618, 765, 1015.
6. Can. P. 162172, 169301, 201480, 201481, 201482; abst. C. A. 1920, **14**, 2398. E. P. 124191; abst. J. S. C. I. 1920, **39**, 450-A. D. R. P. 323961, 1919; abst. Chem. Ztg. 1920, **44**, 421. E. Bergeve and O. Jensen, U. S. P. 1338417; abst. J. S. C. I. 1920, **39**, 450-A; C. A. 1920, **14**, 1873. E. P. 120378; abst. J. S. C. I. 1919, **38**, 817-A. U. S. P. 1324255, 1919; abst. J. S. C. I. 1920, **39**, 108-A. Ital. P. 130372, 1912. For additional data on the problems of nitrogen fixation, see Anon., Nature, 1920, **105**, 201; C. A. 1920, **14**, 2055. Anon., Can. Chem. J. 1920, **4**, 80; C. A. 1920, **14**, 1412. K. Arndt, Chem. Ztg. 1915, **39**, 39. A. Bertrand, Chem. Met. Eng. 1920, **22**, 655. H. Dumars, U. S. P. 749040, 1904. O. Dieffenbach and W. Moldenhauer, D. R. P. Anm. D-22635, 1909. R. Davis and L. Olmstead, J. Ind. Eng. Chem. 1920, **12**, 316; C. A. 1919, **13**, 2975; 1920, **14**, 1413; J. S. C. I. 1920, **39**, 362-A. J. Erlich, Ann. Chim. Analyt. 1920, **2**, 143; abst. J. S. C. I. 1920, **39**, 530-A. Elektrizitätswerk Lanza, Aust. P. Appl. 5578, 1916. A. Glasgow, Chem. Age (N. Y.), 1920, **28**, 155. C. Gilbert, Chem. Met. Eng. 1920, **22**, 443; C. A. 1920, **14**, 1412. British Thomson-Houston Co., E. P. 141864, 1919; J. S. C. I. 1920, **39**, 449-A. J. Harger, E. P. 142874; J. S. C. I. 1920, **39**, 516-A. Hamer, Chem. Met. Eng. 1920, **23**, 2. W. Herz, Zts. physik. Chem. 1920, **94**, 256; C. A. 1920, **14**, 1596. C. Houseman, Chem. Age, 1920, **2**, 198; C. A. 1920, **14**, 1413. "Industriegas" Gesellschaft für Sauerstoff u. Stickstoff-Anlagen m. b. H., Aust. P. 60287; Chem. Ztg. 1913, **37**, 894. C. Jones, Chem. Met. Eng. 1920, **22**, 417; C. A. 1920, **14**, 1482. G. Jones, Quart. J. Economics, 1920, **34**, 391; C. A. 1920, **14**, 2395. C. Linde, U. S. P. 815601, 1906; U. S. P. 795525, 1905. F. Lang, D. R. P. 307651; J. S. C. I. 1920, **39**, 449-A. A. Lamb, Chem. Met. Eng. 1920, **22**, 977; C. A. 1920, **14**, 2238. D. Morf, Jap. P. 34896; C. A. 1920, **14**, 2243. Norsk. Hydro-Elektrisk Kvaestofaktieseskab, E. P. 143850, 143854. Ostdeutsche Kalkstickstoffwerke u. Chem. Fabriken, D. R. P. Anm. O-7007, 1910. Nitrogen Co., Ital. P. 113368, 1910. R. Pictet, U. S. P. 683492, 1901. A. Sinding-Larsen and O. Storm, D. R. P. 249246; Wag. Jahr. 1912, **58**, I, 451; C. A. 1912, **6**, 2983; Ital. P. 117259, 1911. Soc. Generale des Nitrures, Ital. P. 128266. L. Summers, 27th Meeting Amer. Electrochem. Soc., 1915; Chem. Ztg. 1915, **39**, 643. E. Thrupp, U. S. P. 743349, 1903. M. Trautz, Zts. Elektrochem. 1919, **25**, 297; C. A. 1920, **14**, 1467. J. Walker, J. C. S. 1920, **117**, 382; J. S. C. I. 1920, **39**, 445-A; J. C. S. 1920, **118**, ii, 308; C. A. 1920, **14**, 2237. W. West, Elec. Rev. 1920, **76**, 929; C. A. 1920, **14**, 2133. B. Wäser has reported on the technology of nitrogen compounds for 1914; Chem. Ztg. 1915, **39**, 782, 967, 988. The various oxides of nitrogen have been made the subject of the patents or researches of E. Briner and R. Jonas, Helv. Chim. Acta, 1920, **3**, 366. Electrochem. Werke, Ital. P. 118530, 1911; D. R. P. Anm. F-16967, 1911. P. Guye, U. S. P. 1331104, 1331105; abst. J. S. C. I. 1920, **39**, 294-A. K. Kaiser, Swiss P. 59140. S. Barth, D. R. P. 298951, 301352; Chem. Ztg. 1920, **44**, 331. H. v. Kiter, U. S. P. 763461, 1904. E. Lemaire, Belg. P. 248272, 1912. C. Matignon and G. Gire, Bull. Soc. Chim. 1920, **27**, 362; J. S. C. I. 1920, **39**, 485-A. Farbw. vorm. Meister,

H. Pauling,¹ E. Reinau,² C. Rossi,³ Sociedad Iberica del Azoe,⁴

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7. Ital. P. 114081, 1911; Aust. P. Anm. 1311, 1911; abst. Chem. Ztg. 1912, **36**, 10, 141.

1. D. R. P. 305553, 1917; abst. J. S. C. I. 1920, **39**, 294-A. Port. P. 8884, 1913. Span. P. 56260, 1913. For further information on the oxidation of atmospheric nitrogen, consult J. Bloom, U. S. P. 1334590; C. A. 1920, **14**, 1489. C. Burdick, U. S. P. 1339494, 1920; C. A. 1920, **14**, 2058; J. S. C. I. 1920, **39**, 489-A. Chem. Fabr. Griesheim-Elektron, D. R. P. 304322; Chem. Zentr. 1920, **91**, II, 435. E. Collett, Norw. P. 21990, 1911. Salpetersäure-Industrie-Ges., Swiss P. 57531. R. Drawe, Can. P. 202066, 1920. F. Foerster, T. Burchardt and E. Fricke, Zts. ang. Chem. 1920, **33**, 113, 122, 129; J. S. C. I. 1920, **39**, 484-A; C. A. 1920, **14**, 2395. P. Guye, Can. P. 200407, 1920; C. A. 1920, **14**, 2057. F. Gros, Compt. rend. 1920, **170**, 811; Bull. Soc. Chim. 1920, **17**, 569; J. S. C. I. 1920, **39**, 331-A. J. Görlinger, D. R. P. 316253; J. S. C. I. 1920, **39**, 447-A. Gewerkschaft des Steinkohlenbergwerkes Lothringer and M. Kelting, D. R. P. Anm. G-49836, 1919. F. Gerhardt, D. R. P. 321981, 303255, 1915. E. Thomson, U. S. P. 1337106; J. S. C. I. 1920, **39**, 404-A. C. Harding and K. McEachron, Trans. Amer. Electrochem. Soc. 1920, **37**; Proc. Amer. Inst. Elec. Eng. 1920; C. A. 1920, **14**, 2135. E. Herman, D. R. P. 305124; J. S. C. I. 1920, **39**, 404-A. J. Island and E. Coleman, Can. P. 197827; C. A. 1920, **14**, 1489; D. R. P. Anm. J-14693. F. de Jahn, Can. P. 201059, 201060; C. A. 1920, **14**, 2398. C. Kaiser, Port. P. 8049, 1911; E. Kilburn Scott, Ital. P. 134798, 1913. E. Kochendoerfer, Can. P. 202073, 1920. Farbw. vorm. Meister, Lucius & Brüning, Hung. P. Appl. F-2787, 1911; Span. P. 51237, 1911. R. Mewes, D. R. P. 316214; addn. to D. R. P. 298846; J. S. C. I. 1920, **39**, 447-A. H. Nöh, D. R. P. 306451; abst. J. S. C. I. 1920, **39**, 404-A. Nitrogen Products Co., Can. P. 201926. F. Powers, U. S. P. 814918, 1906. H. Pick, Zts. Elektrochem. 1920, **26**, 182; J. S. C. I. 1920, **39**, 416-A. C. Rossi, Ital. P. 128995. F. Russ and L. Ehrlich, D. R. P. Anm. R-35506; D. R. P. 266345, 1912; Aust. P. Appl. 4114, 1911; E. P. 443620, 1912. A. Riedel, Aust. P. Appl. 3025, 3050, 1916. Sociedad Iberica del Azoe, Span. P. 56409, 1913. A. Schloessing, Ital. P. 111641, 1910; 130488, 130489, 1912. Salpetersäure-Industrie-Ges., Aust. P. Appl. 4492, 1911; Hung. P. Appl. S-543, 1910. C. Steinmetz, Chem. Met. Eng. 1920, **22**, 299, 353, 411, 455; J. S. C. I. 1920, **39**, 331-A. R. Stock, Can. P. 169901. H. Woll, D. R. P. 316677; J. S. C. I. 1920, **39**, 404-A. E. Wourtsel, Compt. rend. 1920, **170**, 229; C. A. 1920, **14**, 1793.

2. D. R. P. 305171, 1916; abst. J. S. C. I. 1920, **39**, 487-A; Addition to D. R. P. 299001 and 299007; abst. J. S. C. I. 1920, **39**, 449-A.

3. E. P. 455531, 455532; Ital. P. 128993, 128994; abst. Chem. Ztg. 1913, **37**, 741, 980. The oxidation of ammonia to nitric acid has been the subject of the investigations of J. Baumann, Chem. Ztg. 1920, **44**, 145; J. S. C. I. 1920, **39**, 485-A. N. Busvold, Can. P. 168603. General Chemical Co., E. P. 136158; C. A. 1920, **14**, 1196. A. Henwood, U. S. P. 1347158, 1347159. L. Jones and C. Parsons, D. R. P. Anm. J-19966, 1920. K. Kaiser,

whose process was patented in Spain in 1913, as well as that of

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nothing radically new from those herein described.

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CHAPTER VI.

SULFURIC ACID.¹

History of Sulfuric Acid. Sulfuric acid was not known to the ancients; its preparation is described by the Latin writer calling himself Geber, supposed to have lived in the 8th century, but probably only as late as the 15th.² It is mentioned by Libavius (1595), and Sala (1613), who say that it may be prepared either by distilling green vitriol (FeSO_4), or by burning sulfur in moist vessels. N. le Febre and N. Lemery (1666) added niter to the sulfur, the mixture being deflagrated over water under a glass bell. This method was introduced into England by Drebbel, and in 1740 Ward established a small factory at Richmond, near London, in which the mixture of 4 lbs. of sulfur and 1 ozs. of niter was placed in an iron dish over water and covered by a large glass bell. The mixture was ignited and the fumes allowed to dissolve in the water, when another charge was put in. Acid made in this way was called *oleum vitrioli per campanum*, to distinguish it from that made by the dry distillation of ferrous sulfate. This process presents all the elements of the modern method, since sulfur dioxide, nitrogen oxide, air and water are allowed to react in a closed chamber.

The fragile glass globes were replaced by Roebuck of Birmingham by lead chambers 6 ft. wide, and a works was established at Prestonpans, in Scotland, in 1746, the size of the chambers being gradually increased. Acid so made was called "English Acid." In 1779 the process was introduced into France by Holker, and in 1774 la Folie employed a jet of steam in the chamber.

A considerable advance was possible after the researches of

1. The text portion (large print) of this Chapter, (with the exception of pages 1174-1189, 1376-1380 and 1394-1399), has been written by Professor J. R. Partington, M.B.E., D.Sc., of London University, from data furnished by the author, the notes and references being by the latter. For statements or conclusions appearing in the *text* which are not corroborated or refuted in the *notes*, Professor Partington is responsible.

2. E. v. Lippmann, *Zts. ang. Chem.* 1901, **14**, 646. Kopp, "Geschichte der Chemie," **3**, 303. O. Guttmann, *J. S. C. I.* 1901, **20**, 5. R. Carpenter and W. Reid, *J. S. C. I.* 1901, **20**, 7. C. Winkler, *Zts. ang. Chem.* 1900, **13**, 731. • P. Martell, *Chem. Ind.* 1911, **34**, 205.

Clément and Désormes in 1793, who pointed out that a current of air is necessary, and in 1806 these two chemists gave a correct interpretation of the reactions going on in the chambers, especially the rôle played by the nitrogen oxides.

A continuous process was introduced by Holker into the French works of Chaptal in 1810; sulfur dioxide was produced from sulfur in separate burners, and admitted together with nitrous fumes, air and steam, into the chambers.

The use of iron pyrites (FeS_2) instead of sulfur by Hill of Deptford in 1818, and the invention of the Gay-Lussac and Glover towers in 1835 and 1859 respectively, completed the chamber process as we know it today. The Gay-Lussac tower did not come into actual use until about 1840, and the Glover tower was not employed outside of England until some years after its invention on account, perhaps, of misplaced prejudices. The process of soldering the lead plates of the chambers by means of the hydrogen blowpipe directed on the lead itself—"lead burning"—was introduced in 1838 by de Richemond, and has played an important part in the development of the process.

Sulfuric acid is made almost exclusively from sulfur dioxide, which is produced either by burning sulfur in air, or by roasting metallic sulfides such as iron pyrites, copper pyrites, $\text{Cu}_2\text{S} \cdot \text{FeS}_2$, or zinc blende, ZnS . From SO_2 , sulfuric acid is made by two principal methods: (i) the chamber process, (ii) the contact method.

In the chamber process sulfur dioxide, mixed with excess of air as produced by burning sulfur or sulfide ores, is passed over pots containing niter and sulfuric acid in the flues of the burners, from which nitrogen oxides are generated. (In more recent processes these oxides are produced by the catalytic oxidation of ammonia in a special apparatus, and passed into the chambers.) The gases from the pyrite burners then pass into the Glover tower, down which streams a mixture of weak acid from the chambers and "nitrous vitriol" from the Gay-Lussac tower at the end of the system. The nitrous compounds are decomposed, while the liberated nitrogen oxides pass on, together with steam from the evaporation of the weak acid, into the lead chambers, where steam or water spray is blown in, and sulfuric acid diluted with water is formed as a mist, which falls to the bottom of the

chamber and is called "chamber acid." The acid from the Glover tower is fairly strong and passes to the concentrating plant. The nitrogen oxides leaving the chambers are trapped in the Gay-Lussac tower at the end of the plant, down which strong acid trickles, which, absorbing the nitrogen oxides, produces "nitrous vitriol," which is decomposed in the Glover tower, the nitrogen oxides then re-entering the cycle.

In the contact process, a mixture of sulfur dioxide and air is passed over heated platinum or other catalyst in contact with which the sulfur dioxide is oxidized to sulfur trioxide: $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$. This is then absorbed from the gases by means of fairly concentrated sulfuric acid (not water): $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$.

In 1900 the amount of sulfuric acid made in Great Britain from pyrites was 992,100 tons, and 100,00 tons from sulfur and spent-oxide. In the United States in the same year 863,282 tons of acid were made from pyrites and sulfur, and about 75,000 tons from blende, etc. In Germany 279,356 tons were made in 1882, 659,554 tons in 1898, and about 878,000 tons in 1901. France produced 492,000 tons in 1899, Italy and Austria about 200,000 tons each, Belgium 161,000 tons, Russia 125,000 tons, and Japan 50,000 tons. In 1912 the total production of acid was 1,649,681 metric tons,¹ and in 1913 the German imports exceeded the exports by 65,289 metric tons, most of the imports coming from Belgium.

Prior to the war acid was made in the United States almost exclusively from the gases from roasting pyrites and blende, or by the blast-furnace treatment of Tennessee copper ores. During the war a great increase of output was attained by burning sulfur and Australian zinc-concentrates. In the future it is considered that more acid will be made as an adjunct to metallurgical industries.² During the war large oleum plants were erected

1. G. Lunge, *Zts. ang. Chem.* 1903, **16**, 689; abst. *J. S. C. I.* 1903, **22**, 930. K. Reusch, *Chem. Ztg.* 1914, **38**, 1241; abst. *J. S. C. I.* 1915, **34**, 174.

2. L. Skinner (*Met. Chem. Eng.* 1918, **18**, 82; abst. *J. S. C. I.* 1918, **37**, 141-A; *C. A.* 1918, **12**, 2663) has pointed out that the demand for sulfuric acid in the United States during the war period has stimulated production which, however, has never yet met all requirements. To increase the output from zinc-acid plants brimstone has been added to the ore fed into the burners, (Hegeler kilns) whereby the chamber output has been increased 20%. Australian concentrates are being used and may continue to be used after the war. The production from plants now using or which previously used

in England, and it is evident that unless many of these are shut down, a large over-production of acid will result if an increased output for fertilizer purposes can not be arranged. As a result of war experience it has been demonstrated that for high strength acid such as is necessary in the dye industry, the contact system is the cheapest and most efficient. For low-strength acid as required for fertilizers, the Schroeder-Grillo contact system and the chamber process are about equal in cost of production, but for convenience and ease of working the chamber plant has the advantage.¹

pyrites has also increased, to some extent due to the substitution of brimstone for the now scarcer Spanish ore. There is, however, no commercial advantage, even under present conditions, in doing this. The development of the contact processes in America has been restricted by the onerous conditions of licences and royalties imposed by European patent owners. When fine concentrates are used, the roaster gases carry much undesirable dust. The Cottrell process has failed to work satisfactorily under the very severe conditions of acid plants where it has been tried. The lead tower in chamber plants is giving way to cheaper masonry designs and the stoneware fittings to silicon-iron castings. The increased demand for sulfuric acid has been due to the production of explosives and to the demand of oil refineries, largely caused by the growth of use of motor vehicles under war conditions. The quantity available for the manufacture of fertilizers has been insufficient for the demand. In the future, acid production will be an adjunct to the metallurgical industry. Pyrites and also brimstone burning for acid will probably decline. Much will depend on the transport facilities which should be arranged in the national interest to favor the utilization of the waste and noxious gases produced by smelting works.

1. J. S. C. I. 1918, **37**, 118-R. S. Salisbury, Mineral Industry, 1915, **24**, 642; abst. C. A. 1917, **11**, 188. J. S. C. I. 1902, **21**, 1162; 1916, **35**, 1107. W. Phalen, U. S. Geol. Survey, 1912; J. S. C. I. 1912, **31**, 639. W. Smith (J. S. C. I. 1883, **2**, 440) discusses the sulfuric industries of Japan. Report of Departmental Committee on sulfuric acid, 1919; J. S. C. I. 1919, **38**, 90-R. P. Smith, Min. Res. U. S. 1916, II, 403. "P." Gas World (Coking and By-products Sect.), 1918, **69**, No. 1785, 14; 1919, **70**, No. 1802, 17; No. 1811, 19; **71**, No. 1824, 12; abst. C. A. 1919, **13**, 771, 891, 1722, 2110. For description of the South African sulfuric acid industry see S. Afr. J. Ind. Feb. 1919; abst. J. S. C. I. 1919, **38**, 185-R. German sulfuric acid industry, Weekly Bull. Dept. of Trade and Commerce, Canada, July 14, 1919, abst. J. S. C. I. 1919, **38**, 236-A, 352-A. See also Anon., Nature, 1919, **103**, 67; abst. C. A. 1919, **13**, 1244. U. S. Com. Rep. March 13, 1919; abst. J. S. C. I. 1919, **38**, 195-R. National Sulfuric Acid Assoc., Ltd.; J. S. C. I. 1919, **38**, 194-R. Min. Ind. 1918, **27**, 666; abst. C. A. 1919, **13**, 2738. Manufacture of sulfuric acid in New Zealand, J. S. C. I. 1882, **1**, 172. For earlier processes of sulfuric acid manufacture in England, consult the following English patents, P. Pelletan, 3946, 3998, 1815. T. Hills, V. Haddock, 4263, 1818. P. Philips, 6096, 1831. T. Clark, 7440, 1837. W. Gossage, 7636, 1838. J. Heys, W. Thompson, 7793, 1838. J. Fowler, 7831, 1838. E. Duclos, 8149, 1839. H. Blair, H. Watson, 8465, 1840. F. Hills, G. Hills, 8925, 1841. C. Sautter, 9558, 1842. W. Kneller, 9569, 1842. J. Graham, 9912, 1843. W. Cookson, 10116, 1844. W. Birkmyre, 10320, 1844. J. Gamble, 10416, 1844. E. Jones, 10972, 1845. A. Kartz, 11052, 1846. T. Bell, 11307, 1846. F. Hills, 11326, 1846. J. Jullion, 11425, 1846.

Sulfur,¹ being found in a free state in nature, was known

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to the ancients and employed in fumigating.¹ It is used in immense amounts for the preparation of sulfuric acid, especially since the discovery of the Louisiana deposits in the United States. A considerable quantity of brimstone is also used in the production of sulfur dioxide for the manufacture of paper-pulp.

The production of sulfur in various countries has been stated as follows² (exclusive of the amount produced from alkali waste, 20,000–30,000 tons per annum in Great Britain). See p. 1021.

Occurrence of Sulfur. Native sulfur occurs in large quantities in Sicily, principally on the southern water shed from Etna to Sciatti, mixed with limestone and gypsum. It is also found in Romagna, but less abundantly. Small deposits also occur in the Caucasus,³ in Spain, Greece, Japan (43,155 tons in 1910), Persia, Hawaii,⁴ and Germany,⁵ more important deposits occur in New Zealand (Whale Island),⁶ and especially in Louisiana, U. S. A.

Sulfur in Sicily⁷ occurs stratified with rock, consisting of 1034, R. Witzcek, J. Gasbel. 1903, **46**, 21, 41, 67, 84, 144, 164, 185; Chem. Centr. 1903, **74**, I, 1052. F. Wöhler, Ann. 1853, **86**, 373; Jahr. Chem. 1853, **6**, 324. A. Wüllner, Wied. Ann. Phys. 1877, **1**, 247, 361; abst. Jahr. Chem. 1877, **30**, 168. M. Yegounow, Arch. des Sc. biolog. (St. Petersburg), **3**, 381; Chem. Centr. 1895, **66**, I, 1123. Analyst. 1876, I, 143; Jahr. Chem. 1876, **29**, 970. C. Young, Amer. J. Sci. 1872, (3), **4**, 356; Jahr. Chem. 1872, **25**, 147. V. Zepharovich, Jahr. Geol. Reichs, 1869, **19**, 225. Jahr. Min. 1876, 24. R. v. Zeynek, Tschermaks Mitt. **15**, 192; Chem. Centr. 1896, **67**, I, 217. See Anon., Chem. Met. Eng. 1919, **20**, 186; abst. C. A. 1919, **13**, 772. Rass. min. **29**, 213. Consult also the following patents: F. P. 297767, 316226 and addn. 2188, 320627 and addn. 3632, 330441, 333004 and addn. 2096, 336278, 336661, 345071 and addn. 5575, 351981, 353028, 353830, 353932 and addn. 4890, 354688, 361866, 361874, 364279, 366280, 369089, 370893, 374469, 376543, 377824, 379559, 384907 and addn. 9760, 9761, 387438, 388191, 391109, 394926, 401067, 405096, 408512, 427892, 431241, 439258, 452034, 454990, 456058, 458028, 472956, 477795. D. R. P. 229, 4610, 25771, 30746, 33100, 45725, 139715, 177281, 186332 192472, 192518, 196604, 202349, 205017, 209960, 245570, 262467, 264920, 272475. Aust. P. 10962, 32904, 45892, 55235, 65959. Swiss P. 57935, 69178. Swed. 349, 33840.

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SULFURIC ACID

TABLE IV.—PRODUCTION OF SULFUR IN VARIOUS COUNTRIES FOR THE PERIOD 1906-1914 INCLUSIVE

| | 1906 | 1907 | 1908 | 1909 | 1910 | 1911 | 1912 | 1913 | 1914 |
|----------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Austria-Hungary..... | 15,238 | 24,199 | 17,429 | 12,856 | 15,976 | | | | |
| Chile..... | 4,598 | 2,900 | 2,705 | 4,508 | 2,641 | | | | |
| France..... | 2,713 | 2,000 | 2,189 | 2,900 | 1,272 | | | | |
| Germany..... | 1,178 | 176 | 811 | 1,185 | 1,000 | 1,251 | 50,000 | 50,000 | 50,000 |
| Greece..... | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 | | | | |
| Italy..... | 499,814 | 426,972 | 455,312 | 435,060 | 430,360 | 414,671 | 404,028 | 394,071 | 381,000 |
| Japan..... | 27,589 | 33,329 | 33,419 | 36,319 | 43,155 | | 54,236 | 49,131 | 50,000 |
| Spain..... | 700 | 3,612 | 13,872 | 21,750 | 30,133 | | | | |
| United States..... | 298,704 | 312,931 | 312,700 | 303,000 | 239,699 | 246,300 | 308,328 | 316,575 | 381,018 |
| Total..... | 843,956 | 801,911 | 829,437 | 817,608 | | | 816,612 | 809,777 | 862,996 |

gypsum, limestone and quartz, occasionally in large transparent crystals. Since fused sulfur deposits prismatic crystals which crumble on standing into minute rhombic crystals, the origin of these deposits can hardly be igneous. It is supposed they have been formed by the interaction of volcanic gases: $\text{SO}_2 + 2\text{H}_2\text{S} = 2\text{H}_2\text{O} + 3\text{S}$, or by the reduction of gypsum by organic matter, or bacteria:¹ $2\text{CaSO}_4 + \text{C} = 2\text{CaCO}_3 + 2\text{S} + \text{CO}_2$.²

The native ore as dug contains 15%–25% sulfur, while rock containing less than 8% does not pay for working. It is stacked in lumps in brick kilns, called *calcaroni*, usually built on a sloping hillside, with air-spaces, and covered with powdered ore. A fire is kindled at the bottom, and the heat of combustion of the sulfur, about 30% of which is burnt, serves to fuse the balance, which flows away into wooden moulds. The blocks so formed still contain 3%–5% of rock, and are exported to Marseilles for refining on account of the scarcity of fuel in Italy. This wasteful process has gradually given way to improved methods, as for instance, the Gill kiln. This latter consists of a closed brick chamber, in which the heating is performed in six compartments arranged in a circle. Better utilization of heat is made possible by means of a coke fire in a central cupola. Operating in this manner admits of a recovery of about 75% of the sulfur in the ore.³

In 1867 Payen and Gill proposed to melt out the sulfur by means of superheated steam. The apparatus devised for this purpose by Thomas⁴ (1869) is in use at present to a limited extent

Zts. ang. Chem. 1890, **3**, 56; 1908, **21**, 1946. J. S. C. I. 1890, **9**, 118. Bechhold, Zts. ang. Chem. 1894, **7**, 33. G. Lock and G. Warnford, Pop. Sci. Month. 1885, **26**, 482. A. Frank, Zts. ang. Chem. 1900, **13**, 843. Jungfleisch, Mon. Sci. 1901, **57**, 511. C. Mene, Mon. Sci. 1867, **9**, 400. Chem. Trade J. **35**, 92. G. Oddo, Chem. Ztg. 1908, **32**, 145; 1910, **34**, 505; abst. J. S. C. I. 1908, **27**, 222. Russ. Min. **29**, 129, 147, 161, 243; abst. C. A. 1908, **2**, 1480, 2848; 1910, **4**, 2549; 1909, **3**, 694. G. Bruhn, Chem. Ind. 1910, **33**, 64. Chem. Ztg. 1908, **32**, 457; abst. J. S. C. I. 1908, **27**, 560; C. A. 1908, **2**, 2128; 1909, **3**, 945. For statistics of S production in Sicily, see Min. Ind. of the U. S., 1911. J. S. C. I. 1911, **30**, 955. See also J. S. C. I. 1902, **21**, 1160; 1904, **23**, 684; 1905, **24**, 696; 1910, **29**, 1376.

1. A. Daubree, Compt. rend. 1881, **92**, 101. A. Etard and L. Olivier, Compt. rend. 1882, **95**, 846, 1363. E. Plauchud, Compt. rend. 1882, **95**, 846. C. Leon, Arch. Suikerind. **20**, 209; abst. C. A. 1913, **7**, 2098.

2. J. Habermann, Zts. anorg. Chem. 1904, **38**, 101; abst. Jahr. Chem. 1904, **57**, 406.

3. Chem. Trade J. **14**, 320. Gruenberg, Chem. Ind. 1893, **16**, 211.

4. A. Rocasolano, Rev. real. acad. Sci. Madrid, **8**, 895; abst. C. A. 1911, **5**, 3501. F. Dickert, U. S. P. 298734; 301222. F. Haber, Zts. Elektrochem. 1902, **2**, 347. K. Walter, Chem. Ztg. 1886, **10**, 1199.

in Romagna. The steam extractor consists of large horizontal iron cylinders lagged with wood, 6 m. long and 80-100 cm. diameter. The ore is loaded in on small wagons with perforated bottoms and run in on rails, the door closed, and superheated steam at 130° admitted. Molten sulfur flows into a small receiver at the bottom, and is removed when the extraction is complete. Eight to twelve batches of five tons each can be thus treated daily, and gives a yield of 80%-90% of the total sulfur. In 1903 32% of the Sicilian sulfur was extracted in *calcaroni*, 55% in regenerative furnaces, and 13% in steam extractors, whereas in 1906 66% was extracted in regenerative furnaces. Solution with carbon disulfide has been tried at Naples and Swoszowice with poor ores (15% S) 99% of the sulfur being recovered. This process is no longer in use at Naples.

Sulfur in Louisiana and Texas. Deposits of sulfur at Charles Lake, Louisiana, have been known since 1868, but have only recently been worked by a special process, due to H. Frasch.¹ In Texas, in the Brezos River valley, southwest of Galveston, a large deposit of sulfur has been found, which has been worked since 1913 by the Freeport Sulfur Co., by a process similar to that of Frasch.² In Louisiana the sulfur is struck at a depth of about

1. U. S. P. 461429, 461430, 461431, 1891; abst. J. A. C. S. 1891, **13**, 257. U. S. P. 1008319, 1911; abst. J. S. C. I. 1911, **30**, 1451; C. A. 1912, **6**, 276; Mon. Sci. 1912, **77**, 129. U. S. P. 1152499, 1915; abst. J. S. C. I. 1915, **34**, 1054; Mon. Sci. 1916, **83**, 52. U. S. P. 799642; abst. Chem. Zts. 1906, **5**, 75; J. A. C. S. 1906, 28-R, 229. U. S. P. 800127; abst. Chem. Zts. 1906, **5**, 75. U. S. P. 870620, 988995; abst. C. A. 1911, **5**, 2158. In this connection see also Eng. Min. J. Oct. 16, 1904. E. Hart, J. A. C. S. 1905, **27**, 158. J. Dubbs, U. S. P. 531787, 1895. G. Lunge, Zts. ang. Chem. 1905, **18**, 1009, 1106. J. Ind. Eng. Chem. 1911, **3**, 355; 1912, **4**, 131. A. Mansbach, J. Amer. Pharm. Assoc. 1918, **1**, 163; abst. C. A. 1918, **12**, 743. R. Vail, Eng. Min. J. 1912, **24**, 449. Chem. Ind. 1913, **36**, 9. Mineral Resources of the U. S. 1909, 686. Eng. Min. J. 1904, Oct. 13th. Chem. Trade J. **35**, 395. F. Pough, J. Ind. Eng. Chem. 1912, **4**, 143. Eng. Min. J. Aug. 23, 1902; abst. J. S. C. I. 1902, **21**, 1204. R. Carmichael, U. S. P. 1287878, 1287879, 1918. For decision on Frasch's patents, see H. Mock and A. Blum, Chem. Met. Eng. 1919, **20**, 637.

2. W. Huff, U. S. P. 1184649, 1916; abst. J. S. C. I. 1916, **35**, 839. K. Thomas, Chem. Met. Eng. 1919, **20**, 261. L. De Sincay, U. S. P. 59328, 1866. S. Johnson, U. S. P. 166279, 1875. L. Labois, U. S. P. 485634, 1892. J. McCabe, U. S. P. 635574, 1899. P. Higgins, U. S. P. 738326, 1903. J. Fleming and H. Froehling, U. S. P. 652672, 1900. W. Hall, U. S. P. 1083255, 1913. W. Huff, U. S. P. 1317625, 1919. R. Perry, U. S. P. 1285358, 1919; abst. C. A. 1919, **13**, 251; J. S. C. I. 1919, **38**, 105-A. J. Peters, U. S. P. 1293902, 1919. J. Hyde, Bur. Mines Mineral Invest. Ser. 1919, No. 15, 18; abst. C. A. 1919, **13**, 2111. M. Lalbin, F. P. 333094, and addition 2096, 1903. G. Oddo, Chem. Ztg. 1910, **34**, 505; abst. C. A.

450 ft. The first and thickest bed of sulfur is 108–112 ft. in diameter, while in the northern portion over 500 ft. of sulfur has been reached. The working of these deposits has been rendered extremely difficult by the presence of several hundred feet of quicksand over the sulfur beds, but it was made possible by the Frasch process. In this a boring to the sulfur bed is made, and three other concentric tubes, lined with aluminium, have been sunk. Down the two outer pipes superheated water (155°) is pumped, the heat being sufficient to fuse the sulfur. Air is then forced down the inner pipe, when an emulsion of water, molten sulfur and air-bubbles rises to the surface through the remaining annular space. This passes to large wooden vats, where sulfur of 99.5% purity solidifies. For superheating the water there are installed 130 boilers of 150–300 h. p. each, in sets of 15 to 20 boilers, all oil fired, the total annual consumption of which is about 7,000,000 barrels. The daily consumption of water is stated as 7,000,000 gallons. Each well produces 400–500 tons of sulfur per day; the total average annual production is over 250,000 tons. Electric heating has also been proposed.

Sulfur deposits have also been reported in Peru,¹ British Columbia,² Mexico,³ Chili,⁴ Venezuela, and also in South Africa.⁵

Production of Sulfur from Sulfides. Sulfur was formerly prepared from iron pyrites by distillation in clay retorts: $3\text{FeS}_2 = \text{Fe}_3\text{S}_4 + 2\text{S}$, or by heating in a limited supply of air: $3\text{FeS}_2 + 5\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{SO}_2 + 3\text{S}$.⁶ Other processes have been proposed,⁷ but have not been successful, since it is much more econ-

1910, **4**, 2549. V. Pigott, P. Billingham and C. Stevensen, India P. 3203, 1917. M. Phillips, Belg. P. 134128, 1898. R. Perry, U. S. P. 1285358; abst. C. A. 1919, **13**, 251.

1. Anon., Mineral Industry, 1912, 681.
2. J. S. C. I. 1901, **20**, 1040.
3. Zts. ang. Chem. 1912, **25**, 366. J. S. C. I. 1901, **20**, 1039.
4. Chem. Ind. 1913, **36**, 403. Chem. Ztg. 1915, **39**, 788, 799.
5. Chem. Trade J. 1912, i, 151.
6. F. Haber, Zts. Elektrochem. 1903, **9**, 400. New Jersey Zinc Co., U. S. P. 1103081, 1103082; abst. C. A. 1914, **8**, 3004; Chem. Ztg. Rep. 1915, **39**, 168; Mon. Sci. 1914, **81**, 181. O. Urbasch, D. R. P. 294912, 1915; abst. J. S. C. I. 1917, **36**, 503; Zts. ang. Chem. 1916, **29**, 537; Chem. Ztg. Rep. 1917, **41**, 2; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 193.
7. L. Wright, E. P. 26128, 1911; abst. C. A. 1913, **7**, 1446; J. S. C. I. 1913, **32**, 29. P. Hofmann, Dingl. Poly. 1876, **220**, 332. Soc. de St. Gobain, F. P. 107820, 1875; abst. Mon. Sci. 1876, **18**, 1104. L. Labois, E. P. 9761, 1884; abst. Wag. Jahr. 1886, **32**, 256. Buisine, D. R. P. 73222; abst. Zts. ang. Chem. 1894, **7**, 89; Chem. Centr. 1894, **65**, 1, 1104; Jahr. Chem. 1894, **47**, 398; Wag. Jahr. 1894, **40**, 431; Ber. 1894, **27**, 347; Mon. Sci. 1894, **44**,

omical to burn the pyrites in air for the production of sulfuric acid. If the latter is used in the manufacture of alkali, the sulfur can be recovered by the Chance-Claus process from the alkali-waste (CaS). In other processes proposed, the pyritic ore is burned to sulfur dioxide and the latter reduced by gaseous hydrocarbons to sulfur in presence of a catalyst such as calcium sulfide.¹ In the W. Hall method² the gases formed by roasting pyrites in a special furnace are submitted to the action of steam and a reducing flame rich in hydrogen, a regulated volume of air being admitted (about 1 vol. air to 2 of gas), just sufficient to combine with the reducing gas and the hydrogen and hydrogen sulfide formed in the reaction. The sulfur vapor is withdrawn at a level above the oxygen admission. Sulfides of zinc, copper and lead may also be treated. Both N. Dekker³ and G. Kingsley⁴

55. J. Holloway, E. P. 500, 1131, 1878; abst. J. A. C. S. 1879, **1**, 174, 296; Chem. Ind. 1878, **1**, 318, 384; Wag. Jahr. 1879, **25**, 270. F. Bode, Dingl. Poly. 1879, **232**, 433. A. Smith, Alkali Reports, 1877-1878, 47. Stickney, Eng. Min. J. **65**, 674. J. Swinburne, D. R. P. 134734; abst. Chem. Centr. 1902, **73**, II, 1024; Jahr. Chem. 1902, **55**, 348; Chem. Zts. 1903, **2**, 220; Chem. Ztg. 1902, **26**, 986; Wag. Jahr. 1902, **48**, I, 215; Mon. Sci. 1903, **59**, 71. M. Malzac, D. R. P. 163473; abst. Zts. ang. Chem. 1906, **19**, 346; Chem. Centr. 1905, **76**, II, 1615; Chem. Ztg. 1905, **29**, 1131; Wag. Jahr. 1905, **51**, I, 387; Mon. Sci. 1906, **65**, 149. Fröhling, Fleming and Whitlock, E. P. 10295, 1900. A. Walter, D. R. P. 192518; abst. Zts. ang. Chem. 1908, **21**, 792; Chem. Zentr. 1908, **79**, I, 316; Jahr. Chem. 1905-1908, I, 1512; Chem. Zts. 1908, **7**, 537; Chem. Ztg. Rep. 1908, **32**, 24; Wag. Jahr. 1907, **53**, I, 320. L. Roos, F. P. 354688. E. Lalbin, F. P. 353830; abst. Chem. Zts. 1906, **5**, 76. E. Fleischer, D. R. P. 205017; abst. Chem. Ztg. Rep. 1909, **33**, 27; Wag. Jahr. 1908, **54**, I, 365; Mon. Sci. 1912, **77**, 50; Zts. ang. Chem. 1909, **22**, 458; Chem. Zentr. 1909, **80**, I, 324; Jahr. Chem. 1909, **62**, 468; Zts. Schiess. Spreng. 1909, **4**, 35. Consortium f. Elektrochemische Industrie, D. R. P. 162913; abst. Zts. ang. Chem. 1905, **18**, 1908; Chem. Centr. 1905, **76**, II, 1059; Jahr. Chem. 1905-1908, I, 2475; Chem. Zts. 1906, **5**, 76; Chem. Ztg. 1905, **29**, 1056; Wag. Jahr. 1905, **51**, I, 387; Mon. Sci. 1906, **65**, 178. G. Aarland, Ber. 1880, **13**, 1763; Chem. Ztg. 1880, **4**, 175; Wag. Jahr. 1880, **26**, 211.

1. A. Hoffman, U. S. P. 1273370, 1918; abst. C. A. 1918, **12**, 1915; J. S. C. I. 1918, **37**, 582-A.

2. U. S. P. 1083248 to 1083253; 1133636, 1133637, 1134846. E. P. 20759, 20760, 26365, 26370, 26594, 26595, 1912; abst. J. S. C. I. 1913, **32**, 842, 1009; 1914, **33**, 135, 359. E. P. 8279, 1913; abst. J. S. C. I. 1913, **32**, 742. F. P. 455005, 458028; abst. Zts. ang. Chem. 1913, **26**, III, 573; Eng. Min. J. July 5, 1913; J. Ind. Eng. Chem. 1913, **5**, 955; J. S. C. I. 1913, **32**, 1009, 1156. See Wierum, "U. S. Min. Res. for 1914," 138. British Sulphur Co., Ltd., Aust. P. Ann. A-6907. E. Fleischer, D. R. P. 205017, 1907; abst. J. S. C. I. 1909, **28**, 90. F. Teed, H. Sulman and H. Picard, E. P. 14628, 1911; abst. C. A. 1913, **7**, 222; J. S. C. I. 1912, **31**, 721; Chem. Ztg. Rep. 1913, **37**, 31; Mon. Sci. 1916, **83**, 41. W. Hall, Can. P. 153478, 162082, 162393, 162516, 169850.

3. F. P. 445768; abst. Mon. Sci. 1913, **79**, 175; C. A. 1913, **7**, 1868; Chem. Ztg. Rep. 1913, **37**, 87.

4. U. S. P. 1144480; abst. Chem. Ztg. Rep. 1916, **40**, 170; Mon. Sci. 1916, **83**, 50.

treat the sulfides by wet processes with sulfates and sulfuric acid, or nitric acid, respectively. K. Birkeland¹ submits blends or other sulfides to the action of superheated steam.

In other processes, sulfur dioxide and hydrogen sulfide are produced and allowed to interact. W. Lang and C. Carson² state that the chief reaction is: $2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$, although sulfuric and thionic acids are formed in smaller quantities. The reaction does not occur with the dry gases, and *liquid* water seems to be essential. Colloidal sulfur is formed.³ P. Fritsche⁴ treats SO_2 and H_2S simultaneously or in succession, with a liquid in which aluminium hydroxide or basic aluminium sulfite is suspended, at a temperature of $60^\circ\text{--}70^\circ$. Soluble basic sulfites are formed, with which H_2S gives a precipitate of sulfur and basic sulfate, the latter being converted into acid sulfite by means of SO_2 . The process may be applied to the separation of sulfur from coal gas. W. Feld⁵ treats the gases with a solution of one or several thiosulfates of metals the sulfides of which are soluble in water. For each part of H_2S one part or more of SO_2 must also be present, and if the gases contain ammonia, an additional two parts of SO_2 for each part of ammonia should be added. Polythionates produced by excess of sulfur dioxide are reduced to thiosulfate by basic or reducing substances (e. g. NH_3 or H_2S or both).

In other processes the gases containing SO_2 are passed over incandescent coke, the principal reaction being: $2\text{SO}_2 + 3\text{C} =$

1. U. S. P. 1121606; abst. Chem. Ztg. Rep. 1916, **40**, 163; Mon. Sci. 1915, **82**, 23.

2. W. Lang and C. Carson, Proc. Chem. Soc. 1905, **21**, 158; abst. J. S. C. I. 1905, **24**, 672.

3. H. Debus, J. C. S. 1888, **53**, 278. See also Aktiebolaget Kolloid, E. P. 7238, 1913; abst. J. S. C. I. 1913, **32**, 791. Belg. P. 255143, 1913. F. P. 465058. E. Jungfleisch and L. Brunel, Compt. rend. 1913, **157**, 257; abst. J. S. C. I. 1913, **32**, 826. L. Sarason, D. R. P. 262467, 1912; abst. C. A. 1913, **7**, 3532; Zts. ang. Chem. 1913, **26**, 476; Chem. Zentr. 1913, **84**, II, 552; Chem. Ztg. Rep. 1913, **37**, 438; Wag. Jahr. 1913, **59**, I, 366; J. S. C. I. 1913, **32**, 827.

4. E. P. 25454, 1911; abst. C. A. 1913, **7**, 1589; J. S. C. I. 1913, **32**, 24.

5. E. P. 157, 10147, 1912; abst. C. A. 1913, **7**, 2099, 3538; J. S. C. I. 1913, **32**, 142, 602. F. P. 432590, 457853. D. R. P. 272474, 272475; abst. C. A. 1914, **8**, 2467, 2480; Zts. ang. Chem. 1914, **27**, 337; Chem. Zentr. 1914, **85**, I, 1468; Chem. Ztg. Rep. 1914, **38**, 238, 239; Wag. Jahr. 1914, **60**, I, 290. U. S. P. 1079291, 1127219; abst. C. A. 1914, **8**, 416; Mon. Sci. 1914, **81**, 27; 1915, **82**, 41; Chem. Ztg. Rep. 1914, **38**, 76. F. P. 387438; abst. J. S. C. I. 1908, **27**, 810; 1912, **31**, 128; 1913, **32**, 1156; 1914, **33**, 692.

$2\text{CO} + \text{CO}_2 + 2\text{S}.$ ¹ It is stated that the reaction is quantitative when the gases are kept in contact with coke for five seconds at 1300° .

Sulfur from Sulfates. Large quantities of sulfur occur in minerals in the form of sulfates, especially in calcium sulfate or gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or anhydrite, CaSO_4 . Immense amounts of this sulfur are to be found near Toyah, Texas. Proposals have been made to obtain sulfur from this source. L. Basset² heats a mixture of calcium sulfate and clay to bright redness in the proportions to give SO_2 and a residue of cement. Sufficient carbon may be added to convert a quarter of the sulfate to sulfide, which then reacts with the remaining sulfate: $3\text{CaSO}_4 + \text{CaS} = 4\text{CaO} + 4\text{SO}_2$, followed by: $\text{SO}_2 + 2\text{CO} = 2\text{CO}_2 + \text{S}$. A furnace for carrying on this operation consists of two zones with a reducing and oxidizing atmosphere respectively, the former being obtained by means of carbon monoxide or powdered carbon in an air-blast. R. Wedekind and Co.³ decompose a mixture of calcium sulfate and sand by the heat of burning pyrites mixed with the mass, e. g., 5 parts gypsum, 2 parts sand, and 3 parts granular Spanish pyrites being used.

Sulfur from Sulfur Dioxide. Mention has already been made of the process of reducing sulfur dioxide with carbon or reducing gases, with production of sulfur. Considerable attention has been paid to the recovery of sulfur from smelter gases containing SO_2 by a reduction process called the Thiogen Process, worked by the Pennsylvania Manufacturing Co.⁴ This depends on the

1. W. Lamoreaux, U. S. P. 1169726, 1182915. E. P. 16543, 1915. F. P. 480345, 1915; abst. J. S. C. I. 1916, **35**, 309, 738; 1917, **36**, 138. W. Lamoreaux and C. Renwick, E. P. 2834, 1915. U. S. P. 1140310. F. P. 477795. Scheurer-Kestner, Compt. rend. 1892, **114**, 296. L. Bemelmans, D. R. P. 77335. J. and F. Weeren, D. R. P. 38041. W. Heinrici, Zts. ang. Chem. 1898, **11**, 525. R. Baggaley, U. S. P. 805701. Soc. anon. Metallurgique "Procedes Laval," D. R. P. 196604. F. Carpenter, U. S. P. 871912, 925751. P. Smith, U. S. P. 878569, 945111, 945112. See also Chem. Ztg. 1886, **10**, 1039; abst. J. S. C. I. 1886, **5**, 534.
2. F. P. 428019, 1910; 466518; E. P. 17873, 1913; abst. J. S. C. I. 1911, **30**, 1452; 1914, **33**, 965.
3. U. S. P. 1008847, 1911; F. P. 419871; abst. J. S. C. I. 1911, **30**, 210, 1452. See also Goldmann, Metall u. Erz. 1919, **16**, 41; abst. C. A. 1919, **13**, 2176. I. and F. Weeren, D. R. P. 38014; abst. Wag. Jahr. 1887, **33**, 488. For the recovery of sulfur from niter cake, see I. Llewellyn and P. Spence and Sons, E. P. 103689; abst. J. S. C. I. 1917, **36**, 385. C. Hansen, U. S. P. 1101740, 1914. Farbenfabr. vorm. F. Bayer & Co., Belg. P. 258963, 1913.
4. S. Young, U. S. P. 1094656, 1094767. F. P. 450786. D. R. P.

reduction of sulfur dioxide by ethylenic hydrocarbons: $3\text{SO}_2 + \text{C}_2\text{H}_4 = 3\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O}$. The reaction, which is very incomplete and slow, may be accelerated by the use of a catalyst such as ferric oxide or calcium sulfide. The latter probably acts as follows: (1) $2\text{CaS} + 3\text{SO}_2 = 2\text{CaCO}_3 + 3\text{S}$; (2) $2\text{CaCO}_3 + \text{C}_2\text{H}_4 = 2\text{CaS} + 2\text{CO}_2 + 2\text{H}_2\text{O}$. The roaster gases, containing about 8% SO_2 , pass through a dust separator to a combustion chamber, where a limited amount of oil is introduced and the excess of oxygen consumed. The gases next pass to the combustion chamber, where a further supply of oil is added, in quantity sufficient to remove the oxygen from the SO_2 . The contact mass is made up with plaster of Paris and iron salts. The chief difficulty appears to be deterioration of the contact mass by the high temperature and dust. The temperature in the contact chamber is about 800° , the oil being introduced in the form of a spray. By this process it is stated that the sulfur content of the gases may be reduced to 0.2%. Other reduction processes have been proposed.¹ The claim is put forth that the thiogen process is likely to be economically successful only when sulfuric acid cannot be made directly from the gases.²

If sulfites are made from SO_2 they may be treated for the production of sulfur by heating under pressure with a little water:³ $2\text{NaHSO}_3 + \text{Na}_2\text{SO}_3 = 2\text{Na}_2\text{SO}_4 + \text{S} + \text{H}_2\text{O}$. About 3%-4% of polythionates may also be added and the heating conducted in an open vessel.⁴

Sulfur from Alkali Waste. In the preparation of soda by

271002. See U. S. Min. Res. for 1914, 139; Chem. Ztg. 1914, **38**, 383; J. S. C. I. 1912, **31**, 602; 1914, **33**, 593. Met. Chem. Eng. 1917, **16**, 309; abst. J. S. C. I. 1917, **36**, 506. A. G. für Bergbau, Blei u. Zinkfabrikation zu Stolberg, D. R. P. 253493; abst. J. S. C. I. 1913, **32**, 23. See also F. Wilson, Chem. Ztg. Rep. 1912, **36**, 514.

1. W. Hall, E. P. 26594, 1912. S. Young, U. S. P. 1262295, 1915; abst. J. S. C. I. 1918, **37**, 333-A. P. Smith, U. S. P. 878569, 1908; abst. J. S. C. I. 1908, **27**, 282. F. Teed, H. Sulman and H. Picard, E. P. 14628, 1911; abst. J. S. C. I. 1912, **31**, 721. Soc. anon. metallurgique "Procédes de Laval," Wag. Jahr. 1908, **54**, I, 366.

2. C. Schiffner, Chem. Ztg. 1914, **36**, 9, 16, 383; Metall u. Erz, 1914, **11**, 257; abst. J. S. C. I. 1914, **33**, 1160.

3. Farb. vorm. F. Bayer & Co., D. R. P. 265167, 1912; abst. J. S. C. I. 1913, **32**, 1068.

4. Farb. v. F. Bayer & Co., U. S. P. 1102911, 1914; F. P. 459713, 1913; D. R. P. 263167, 264920, 265167; abst. J. S. C. I. 1913, **32**, 1068, 1109. W. Feld, U. S. P. 1127219, 1915; E. P. 10147, 1912; D. R. P. Anm. of March 7, 1912; abst. J. S. C. I. 1913, **32**, 602; 1915, **34**, 283. Belg. P. 217695, 1909. F. P. 408253, 1909. Swiss P. 42330, 1908. See also L. Bassett,

the Leblanc process, the sulfur contained in the sulfuric acid used in making saltcake is left in the so-called alkali waste in the form of calcium sulfide. About 40% of this waste consists of CaS, and in the early days of the industry, when this was not utilized, large amounts of sulfur were thus lost. In Great Britain it is estimated that 150,000 tons of sulfur, valued at \$2,000,000, were in this manner, annually run to waste. The utilization of this waste was a pressing problem for the old Leblanc industry, and its successful solution has enabled that process still to be carried on as a source of caustic soda. Gossage in 1838, decomposed the waste by carbon dioxide, with production of hydrogen sulfide: $\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{S}$, but this has been improved by A. Chance.¹ The suspension of the waste is treated with limekiln gas, as free from carbon monoxide and oxygen as possible, in a number, say seven, of large iron cylinders called carbonators, 15 ft. by 7 ft. As the H_2S evolved is diluted with too much nitrogen to be directly utilizable, it is passed into another carbonator of waste, where the H_2S is absorbed as hydrosulfide: $\text{CaS} + \text{H}_2\text{S} = \text{Ca}(\text{SH})_2$, the nitrogen passing off. If kiln gas is now passed through this hydrosulfide, H_2S diluted with only half as much nitrogen as before is obtained, and collected in large gasometers: $\text{Ca}(\text{SH})_2 + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + 2\text{H}_2\text{S}$.

The H_2S is then passed to the Claus kiln where, after admixture with the proper proportion of air, it passes over shelves on which is spread hydrated porous iron oxide, in presence of which as a catalyst, the following reaction occurs: $2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{S}$. The sulfur is condensed in brickwork chambers in a very pure state, up to 80% being recoverable. The proportions of H_2S and SO_2 in the exit gases are regulated throughout the process, and the temperature of the kilns is kept low. The exit gases should be kept at about 290° one foot from the kiln.² It has been proposed³ to convert gypsum into CaS by reduction with

E. P. 20716, 1915; abst. J. S. C. I. 1915, **34**, 28. M. v. Schaffner and W. Helbig, D. R. P. 4610, 6895; abst. Wag. Jahr. 1879, **25**, 273. P. Smith, U. S. P. 912743, 912744, 1909. M. Rotten, D. R. P. 74525; abst. Wag. Jahr. 1894, **40**, 430. Oester. Sodafabrik, D. R. P. 30746; abst. Wag. Jahr. 1885, **31**, 206. C. Maybluch, Belg. P. 160067, 1901. T. Montgomery and J. Warnke, U. S. P. 433534, 1890. See also E. Heinze, J. prakt. Chem. 1919, **99**, 109; abst. J. S. C. I. 1919, **38**, 573-A. C. Collins, U. S. P. 1314634, 1919; abst. J. S. C. I. 1919, **38**, 861-A.

1. J. S. C. I. 1888, **7**, 162.

2. R. Carpenter and S. Lindner, J. S. C. I. 1903, **22**, 457; 1904, **23**, 557.

3. E. Hilde, Rev. prod. chim. 1918, **21**, 165; abst. C. A. 1918, **12**, 2414.

carbon, and then treat according to the Chance-Claus process for recovery of sulfur. Schaffner and Helbig have proposed to treat CaS in closed vessels with a solution of MgCl_2 , the reaction being: $\text{CaS} + \text{MgCl}_2 + 2\text{H}_2\text{O} = \text{CaCl}_2 + \text{Mg}(\text{OH})_2 + \text{H}_2\text{S}$. The success of such processes, involving endothermal reduction of sulfates with carbon, depends in a large measure on the price of coal.¹ Treatment of niter cake and glauberite residues by this reaction is possible. Various other processes have been put forward,² but have not been successful, as far as can be ascertained, the Chance-Claus process alone being worked.

Other Sources of Sulfur. An important source of sulfur is that contained as pyrites in coal³ used for the manufacture of illuminating gas. In the crude gas it is evolved in the form of H_2S and CS_2 . The former is removed by passage over hydrated iron oxide as in the Claus process, except that the mass is not heated. The FeS produced is reoxidized by exposure of the mass

1. Cf. J. Partington, "Alkali Industry," 1918, 63.
2. H. Blair, E. P. 313, 1858. J. Townsend and J. Walker, E. P. 1647, 1860. M. Schaffner and W. Helbig, E. P. 3186, 1882. M. Helbig, U. S. P. 1315496, 1919. H. Kenyon and I. Swindells, E. P. 79, 1871. A. Carey, O. Heslop and The United Alkali Co., E. P. 10351, 1902; abst. J. S. C. I. 1903, **22**, 553. See also W. Baranoff, E. P. 7269, 1898. Chem. Fabrik Rhenania and F. Projahn, D. R. P. 173239. See Chem. Ztg. 1908, **32**, 247. C. Tyers, J. Hedley and The United Alkali Co., E. P. 25976, 1906. G. Hellsing, D. R. P. 209960; F. P. 376534; E. P. 8164, 1907. E. Burschell, E. P. 11133, 1906. Gewerkschaft Messel, D. R. P. 181063. K. Burkheiser, D. R. P. 220632. Nürnberger Consortium f. elektrochem. Industrie, D. R. P. 162913. S. Palaschkowski, Russ. P. 5464, 5477, 1901; abst. Chem. Ztg. 1902, **26**, 15. A. Müntz and P. Nottin, F. P. 375469. W. Feld, E. P. 3061, 1909. U. S. P. 985667. D. R. P. 192533, 237607. E. P. 2719, 1908. U. S. P. 927342. D. R. P. 202349. F. P. 387438. Belg. P. 254420, 1913; 205943, 1908. A. Gutensohn, U. S. P. 709842, 1902. E. Müller, E. P. 15272, 1902; abst. J. S. C. I. 1903, **22**, 913. C. Malsch and C. Gilson, U. S. P. 4303701; abst. C. A. 1919, **13**, 1815. G. Leckie, U. S. P. 202443, 1878. J. Hollway, U. S. P. 234129, 1880. Harbord, E. P. 124266; abst. J. S. C. I. 1919, **38**, 239-A. W. Weldon, D. R. P. 1764; E. P. 444, 445, 1877; abst. Chem. Ind. 1878, **2**, 49, 265; Ber. 1877, **10**, 1976; 1878, **11**, 265; Bull. Soc. Chim. 1878, **29**, 141, 191; Wag. Jahr. 1878, **24**, 380. E. Parnell and J. Simpson, D. R. P. 33255, 35122, 35232, 39667; abst. Wag. Jahr. 1885, **31**, 245; 1886, **32**, 287, 288; 1887, **33**, 533; 1888, **34**, 437; Mon. Sci. 1889, **33**, 955; 1891, **38**, 641. F. Rawes, D. R. P. 25771; abst. Wag. Jahr. 1884, **30**, 266. C. Opl, D. R. P. 23142; abst. Wag. Jahr. 1883, **29**, 258; Mon. Sci. 1890, **35**, 118; Chem. Ind. 1883, **6**, 232. H. v. Miller and C. Opl, D. R. P. 28067; abst. Wag. Jahr. 1884, **30**, 307. H. Leith, D. R. P. 57642; abst. Wag. Jahr. 1891, **37**, 370. J. Kynaston, D. R. P. 34825; abst. Wag. Jahr. 1886, **32**, 286. W. Helbig, D. R. P. 20948. E. Hildt, B. de Montenegro and J. Lasnier, Belg. P. 167364, 1902. H. Grouven, D. R. P. 29848; abst. Wag. Jahr. 1884, **30**, 1218; Mon. Sci. 1885, **27**, 484. G. Lunge and J. Dewar, U. S. P. 480109, 1892. D. Hewitt, E. P. 697, 1877.
3. T. Drakeley, J. C. S. 1916, **103**, 723.

to the air, with the formation of sulfur: $2\text{Fe}(\text{OH})_3 + 3\text{H}_2\text{S} = 2\text{FeS} + 6\text{H}_2\text{O} + \text{S}(\text{removal of S})$; $4\text{FeS} + 3\text{O}_2 + 6\text{H}_2\text{O} = 4\text{Fe}(\text{OH})_3 + 4\text{S}(\text{revivification})$. When the mass contains up to 40%–50% S it is removed from the purifiers, and is then called "spent oxide." Many proposals for the recovery of sulfur from spent oxide have been made.¹ The mass contains a variable amount of tarry matter, and inasmuch as sawdust is usually mixed with the iron oxide to increase the porosity, it contains this organic matter. Simple distillation, therefore, is useless. The proposition has been made to extract the sulfur with solvents such as carbon disulfide, with or without previous destruction or removal of the tar, but the usual process is to burn the spent oxide in a rotary kiln or mechanical burner to SO_2 , and use this in the manufacture of sulfuric acid. The sulfur made from spent oxide is usually impure and contains tarry matter. This may be re-

1. J. Becigneul, F. P. 345071, 1904 and additions thereto; abst. J. S. C. I. 1904, **23**, 1216; 1905, **24**, 1067; 1906, **25**, 583, 985. K. Burkheiser, U. S. P. 1018479, 1912. F. Bauke, E. P. 28280, 1907; abst. J. S. C. I. 1908, **27**, 1144. Chemische Industrie Aktien Ges. and F. Wolf, D. R. P. 248001. E. Ciselet and C. Deguide, D. R. P. 288767. Belg. P. 259087, 262142, 1913. H. Gouthiere et Cie. and P. Ducaneel, E. P. 13383, 1911; F. P. 427892, 434673 and first addition thereto, dated May 2, 1911; abst. J. S. C. I. 1911, **30**, 1151; 1912, **31**, 324, 816. Belg. P. 235885, 1911. Swiss P. 57935; abst. Chem. Ztg. 1913, **37**, 163. E. Hunt and W. Gidden, U. S. P. 1059996, 1913; E. P. 8097, 1912; F. P. 452034, 1912; abst. J. S. C. I. 1913, **32**, 602, 603, 657. H. Koppers, E. P. 21385, 1913. J. Mackenzie, E. P. 4770, 1913. E. Murphy, Amer. Gas Inst. 1916; J. Gaslighting, 1916, **136**, 396; abst. J. S. C. I. 1916, **35**, 1209. Norddeutsche Präparaten Fabr. Heydorn & Biegel, D. R. P. 305418, 1917; abst. J. S. C. I. 1918, **37**, 467-A. Soc. d'Eclairage, Chauffage et Force Motrice, F. P. 454990, 1913; abst. J. S. C. I. 1913, **32**, 868. Soc. Anon. d'Exploitation des Proc. Becigneul and E. Berger, F. P. 391109, 1907; abst. J. S. C. I. 1908, **27**, 1112. P. Williams, E. P. 596, 1909; abst. C. A. 1909, **3**, 2493. See also, J. S. C. I. 1883, **2**, 491. G. Gerlach, D. R. P. 229, 1877; abst. Wag. Jahr. 1879, **25**, 268; 1882, **28**, 234. O. Ross, E. P. 713, 1879; cf. Sci. Amer. 1879, **39**, 276; Chem. Ztg. 1879, **3**, 241. C. Dubois, E. P. 13108, 1885; 7129, 1886. D. R. P. 41718. Broadberry, Gas World, 1895, **23**, 643. J. Becigneul, D. R. P. 178020; E. P. 8530, 1905. A. Cornillaux, E. P. 7616, 1905; Belg. P. 185791, 1905. C. Maybluh, D. R. P. 148124. E. Vaton and A. Zuaznavar, F. P. 336661. E. Günther and R. Franke, E. P. 11187, 1907; F. P. 377827. A. Derome, F. P. 372099. Other processes are, K. Burkheiser, D. R. P. 235870. W. Feld, D. R. P. 272474, 272475; abst. Zts. ang. Chem. 1914, **27**, II, 337. P. Fritzsche, D. R. P. 250243, 251353. Soc. H. Gouthiere, D. R. P. 245570; abst. C. A. 1912, **6**, 2311. Akt. Ges. f. Chem. Industrie and F. Wolf, D. R. P. 248001; abst. C. A. 1912, **6**, 2684. See E. Espenhahn, J. S. C. I. 1916, **35**, 292. H. Köhler, U. S. P. 898378, 1908; abst. J. S. C. I. 1908, **27**, 982. F. P. 379559, 1907; abst. J. S. C. I. 1907, **26**, 1252. Craig and Spence & Sons, E. P. Appl. 17691, 1918; abst. J. S. C. I. 1918, **37**, 721-A. W. Anderson, E. P. 127128, 1918; abst. J. S. C. I. 1919, **38**, 399-A. P. Austin, U. S. P. 1315940; abst. J. S. C. I. 1919, **38**, 861-A. •

moved, as¹ by filtering the solution in benzene or toluene through animal charcoal. It is impossible to separate the solvent from the sulfur by simple distillation. To effect this it has been proposed² to run the CS₂ solution into water at 70°, so that the solvent may be volatilized. J. Cobb³ passes crude gas, containing H₂S and ammonia, through a solution of zinc or manganous sulfate at 80°, whereby ammonium sulfate and the corresponding sulfides are formed. After filtration, the ammonium sulfate is crystallized out and the sulfides are roasted with production of sulfates and a residue containing sulfides. This is suspended in water and treated with sulfur dioxide from the previous roasting, to produce soluble sulfites, which are utilized in further treatment of the gas.

Proposals have also been made for the treatment of smelter gases, containing SO₂ (see p. 1082). These may be treated with a solution of calcium sulfide, with precipitation of sulfur.⁴ This is the principal of the Wet Thiogen Process.⁵ When calcium or barium sulfide solution is used the following reactions occur: (1) $2\text{CaS} + 3\text{SO}_2 = 2\text{CaSO}_3 + 3\text{S}$, or (2) $2\text{CaS} + 3\text{SO}_2 = 2\text{CaS}_2\text{O}_3 + \text{S}$. The sulfur dioxide is removed from the gases by solution in water, and the powdered sulfide added. The precipitate containing sulfide, thiosulfate and sulfur is settled, and the mother liquor used for absorption of SO₂. The precipitate is dried and distilled, when the free S and half the sulfur in the thiosulfate is recoverable. The residue may be reduced to sulfide by heating with carbon and used again. The process, which has been a success in the laboratory tests, may be useful in certain localities.

Proposals for the recovery of sulfur from sulfite cellulose lyes have been made.⁶

Sublimed Sulfur. The major portion of crude sulfur mined

1. J. Becigneul, D. R. P. 178020; abst. Wag. Jahr. 1906, **52**, I, 58; Chem. Centr. 1906, **77**, II, 1743. Belg. P. 186019, 1905.

2. Chem. Fabrik Phoenix, Rohleder & Co., D. R. P. 182820. E. P. 23957, 1906. F. P. 370893; abst. Wag. Jahr. 1907, **53**, I, 324; Chem. Zentr. 1907, **78**, II, 651. Belg. P. 195474, 1906.

3. J. Cobb, F. P. 458788, 1913; E. P. 13141, 1912; abst. J. S. C. I. 1913, **32**, 971, 1059. See also F. Duviolsart, Belg. P. 232115, 1911.

4. H. Sanborn, H. McMahon, J. Overbury and S. Young, U. S. P. 1062120, 1913; E. P. 18202, 1911; abst. J. S. C. I. 1912, **31**, 287; 1913, **32**, 657.

5. The Wet Thiogen Process for recovering sulfur from sulfur dioxide in smelter gases by A. Wells, Bull. 133, Bureau of Mines, U. S. A. 1917. See also C. Fulton, Bull. 84, Bur. of Mines, 1915, 72. F. Schönfeld, Ann. 1855, **95**, 1.

6. R. v. Walther, D. R. P. 262468, 1912; abst. J. S. C. I. 1913, **32**,

in Sicily is exported to Marseilles for refining by the Michel process, since fuel is too expensive in Italy.¹ The sulfur is melted and run into iron retorts, heated over a fire. The retort communicates with a large brickwork chamber into which the vapor passes. At first the vapor condenses on the cold walls as a light yellow powder, called Flowers of Sulfur.² As the walls become hot the sulfur condenses in the liquid form, and collects at the bottom of the chamber, whence it is tapped off into wooden moulds to form the sticks of Roll Sulfur. Such an apparatus produces about 2 tons of refined sulfur per 24 hours, with the use of about half a ton of coal. Sulfur is also refined in Germany, and some in Italy at Romagna and Catania.³ Flowers of sulfur 827; C. A. 1913, **7**, 3663; Wag. Jahr. 1913, **59**, 1, 366. In this connection see also S. Young, Eng. Min. J. 1913, **95**, 369; abst. J. S. C. I. 1913, **32**, 293. R. Lal Datta, U. S. P. 1313370, 1919. India P. 3775, 1918. J. Kircher, U. S. P. 137692, 1873. S. Coulier (Belg. P. 210951, 1908) recovers sulfur from wastes arising from the manufacture of artificial silk. For the recovery of sulfur contained in petroleum, see H. Blackmore, U. S. P. 793026, 1905; abst. J. A. C. S. 1906, **28**, 79. H. Baker, U. S. P. 86201, 1869. For the method of determining sulfur in spent oxide, see N. Twisselmann, Chem. Ztg. 1918, **42**, 588. The extraction of sulfur from its ores by heating and centrifuging is described by A. Sedgewick, U. S. P. 1318015; abst. J. S. C. I. 1919, **38**, 901-A. Cf. W. Huff, U. S. P. 1317625; abst. J. S. C. I. 1919, **38**, 901-A.

1. Muspratt, Tech. Chem. 1900, **7**, 1089.

2. F. Janda, Wag. Jahr. 1898, **44**, 421. A. Domergue, Chem. Ztg. Rep. 1905, **29**, 19. Chem. Centr. 1906, **77**, 1, 8. French Agricultural Society, Chem. Centr. 1905, **76**, II, 1482. R. Marcille, Ann. Chim. Appl. 1906, **10**, 1011; Zts. ang. Chem. 1906, **19**, 99. Taurel and Griffet, Compt. rend. 1911, **152**, 1182; abst. J. S. C. I. 1911, **30**, 683. See also E. Bert, F. P. 401023. H. Niedenführ, D. R. P. 249330. For the composition of flowers of sulfur, see L. Prunier, Chem. Centr. 1896, **67**, I, 279. E. Tittinger, Pharm. Post, 1897, **27**, 297; abst. Chem. Centr. 1894, **65**, II, 267. N. Leonard, Analyst, 1901, **26**, 319. A. Harpf, Zts. anorg. Chem. 1904, **39**, 3870. Windisch, Landw. Jahr. **30**, 497. P. Antoine, D. R. P. 45725; abst. Wag. Jahr. 1889, **35**, 359.

3. G. de Bechi and S. Bornett, Belg. P. 256428, 1913. R. Davidson and United Alkali Co., E. P. 17476, 1897; 7088, 1898. A. Walter, D. R. P. 177281, 192471, 192472. U. S. P. 873812. Soc. Anon. metallurgique, "Procédes de Laval," D. R. P. 168870. Boude et Fils, F. P. 361874, 369089. E. Rasse-Courbet, F. P. 366280. A. Dementieff, F. P. 351981. A. Consoli, E. P. 8757, 1902; F. P. 316226. A. Scott and A. Meyer, F. P. 439258; abst. C. A. 1912, **6**, 3501. Belg. P. 242522, 1912; Ital. P. 122739; abst. Chem. Ztg. 1913, **37**, 32. W. Hall, E. P. 26594, 1912. T. Hashiride and T. Takane, Jap. P. 32100, 1918; abst. C. A. 1918, **12**, 2239. A. Alonzo-Consoli, Belg. P. 159891, 1901; 172241, 1903. C. Dubois, U. S. P. 420719, 1890. F. Dickert, U. S. P. 310187, 1885. G. Dexter, U. S. P. of Oct. 6, 1806. H. Eames, U. S. P. 204206, 1878. E. Frazier, U. S. P. 182362, 1876. H. Hillyer, U. S. P. 1048161, 1912. J. Lagache, Belg. P. 190840, 1906. G. Robertson, U. S. P. of Nov. 16, 1812. E. White, U. S. P. 443629, 1890. D. Paynter, U. S. P. 23141, 1859. See also Noyer, Caoutchouc and Gutta, 1918, **15**, 9661; abst. C. A. 1919, **13**, 528. J. Scott, Chem. Trade J. 1919, **65**, 443; abst. J. S. C. I. 1919, **38**, 861-A.

have also been replaced to some extent by finely ground and sieved sulfur.¹ The fineness of these powders is estimated by the Chancel sulfurimeter,² which consists of a glass tube in which the sulfur is shaken with ether, and the depth of the deposits noted. The results are given in "Degrees Chancel."

Special processes for obtaining finely divided³ and colloidal sulfur have been described.⁴

Properties of Sulfur. General properties are the boiling point, which is 444.61° according to N. Kumoropoulos⁵ and Chappui, 444.8° and 443.58° according to others; and the atomic weight, which is 32.065 (O = 16) according to T. Richards and C. Hoover.⁶

As regards some ill-defined properties, it may be stated that sulfur is appreciably volatile at 100°.⁷ When heated gently it phosphoresces,⁸ and at a higher temperature takes fire.⁹ The ignition point in air is given as 360°, in oxygen 275°–280°. The free energy of the different varieties of sulfur has been studied by G. Lewis and M. Randall.¹⁰

Sulfur occurs in two crystalline modifications, rhombic or α -sulfur, and monoclinic or β -sulfur. The transition point of

1. A. Walter, D. R. P. 136547. Ducancel, Gouthiere & Co., F. P. 401067. R. Marcell, Chem. Ztg. 1911, **35**, 426. J. Fabre, F. P. 437015. H. Fonze-Diacon, Ann. Falsif. 1916, **9**, 333; abst. J. S. C. I. 1917, **36**, 338.
2. See Zts. anal. Chem. 1906, **45**, 760; Vinassa, Staz. Esper. agrar. 1916, 188.
3. H. Köhler, D. R. P. 192815, 1906; abst. J. S. C. I. 1908, **27**, 503. U. S. P. 898378. See also J. Amiot, Belg. P. 161845, 1902. P. Claes, Belg. P. 183371, 1905.
4. Chem. Fabrik. von Heyden, D. R. P. 201371, 1907; abst. J. S. C. I. 1908, **27**, 1132. M. Raffo and J. Mancini, Zts. Chem. Ind. Koll. 1911, **9**, 58; abst. J. S. C. I. 1911, **30**, 1114.
5. Proc. Roy. Soc. 1914, **90**, 189; abst. C. A. 1914, **8**, 2295. L. Holborn and E. Grüneisen, Ann. Phys. 1901, **6**, 123. H. Callendar, Proc. Roy. Soc. 1908, **81-A**, 329; abst. Jahr. Chem. 1905–1908, I, 1514.
6. J. A. C. S. 1915, **37**, 108; abst. J. C. S. 1915, **108**, ii, 96.
7. P. Jones, Proc. Manchester Lit. and Phil. Soc. 1911, 14; abst. J. S. C. I. 1912, **31**, 815. J. Moss, J. C. S. 1907, **92**, ii, 20. J. Dewar, Proc. Roy. Soc. 1865, **14**, 7. Matthies, Phys. Zts. **7**, 395. H. Grüner, Science, 1905, 74; Zts. ang. Chem. 1905, **18**, 1907; J. A. C. S. 1907, **29**, 1396. Zts. anorg. Chem. 1908, **56**, 145. O. Ruff and H. Graf, Ber. 1907, **40**, 4199. T. Porter, Proc. Chem. Soc. 1898, 65.
8. L. Bloch, Compt. rend. 1909, **148**, 782; Ann. Chim. Phys. 1911, **22**, 460. W. Watson, Chem. News, 1913, **108**, 187.
9. H. Moissan, Compt. rend. 1903, **137**, 547; abst. J. S. C. I. 1903, **22**, 1193. R. McCrea and A. Wilson, Chem. News, 1907, **95**, 169; **96**, 25, J. Hill, Chem. News, 1907, **95**, 169. K. Friedrich, Chem. Zentr. 1909, **80**, II, 316. J. Kastle and J. McHargue, Amer. Chem. J. 1907, **33**, 466.
10. J. A. C. S. 1914, **36**, 2259; abst. J. C. S. 1915, **108**, ii, 12.

rhombic to monoclinic sulfur is 94.5° ;¹ below this temperature rhombic sulfur is stable, above it, monoclinic sulfur. The transition takes place somewhat slowly, so that if rhombic sulfur is quickly heated it fuses at its proper melting point of 111.5° , but if kept for some time at 108° it is converted into the monoclinic variety which then fuses at 120° . The densities of the two forms are also different, that of rhombic sulfur being 2.06, and of monoclinic, 1.98. Both forms are soluble in CS_2 .

When ordinary sulfur is heated it first forms a clear mobile liquid of a pale yellow color, but on continued heating becomes viscous and dark. If the boiling liquid is poured into cold water a sticky, soft mass, called plastic sulfur, is obtained, which on standing becomes yellow, opaque and brittle, owing to its conversion into minute rhombic crystals. This form appears not to be produced if the sulfur is quite pure,² and would appear to consist of more than one kind of sulfur; two kinds of liquid sulfur called S- λ and S- μ , are recognized, but there may be others,³ as R. Engel⁴ has described another crystalline modification. A blue variety of sulfur appears also to exist.⁵ Other forms have been noticed,⁶ the subject being really one of considerable complexity.

1. E. Beckmann, R. Paul and O. Liesche, Zts. anorg. Chem. 1918, **103**, 189; abst. C. A. 1919, **13**, 2787.

2. R. Threlfall, J. Brearley and J. Allen, Proc. Roy. Soc. 1894, **56**, 32; abst. Jahr. Chem. 1894, **47**, 400.

3. A. Smith, W. Holmes and E. Hall, Zts. physik. Chem. 1903, **42**, 469; 1905, **52**, 602; abst. J. A. C. S. 1905, **27**, 797; Chem. Centr. 1903, **74**, I, 274; 1905, **76**, II, 601. A. Smith and W. Holmes, Zts. physik. Chem. 1906, **54**, 257; abst. J. A. C. S. 1905, **27**, 979. A. Smith and C. Carson, Zts. physik. Chem. 1905, **52**, 685; abst. J. C. S. 1907, **92**, ii, 208. C. Carson, J. A. C. S. 1907, **29**, 499. R. Brownlee, J. A. C. S. 1907, **29**, 1032. A. Smith and C. Carson, Zts. physik. Chem. 1911, **77**, 661; abst. J. C. S. 1911, **100**, ii, 977. W. Spring, Naturwissen. Rundschau, 1906, 494. G. Quincke, Ann. Phys. 1908, (4), **26**, 625. M. Domergue, J. pharm. chim. 1904, **20**, 493. M. Raffo, J. S. C. I. 1908, **27**, 747.

4. Compt. rend. 1891, **112**, 866. A. Aten, Zts. physik. Chem. 1913, **83**, 442; 1914, **88**, 442; abst. Chem. Ztg. Rep. 1914, **38**, 247; J. C. S. 1915, **108**, ii, 254; J. S. C. I. 1914, **33**, 1087; 1915, **34**, 659.

5. E. Paterno and A. Mazzuchelli, Atti R. Accad. dei Lincei Roma, 1907, **16**, I, 465; abst. Chem. Centr. 1907, **78**, II, 11; J. C. S. 1907, **92**, ii, 451. P. Weimarn, J. Russ. Phys. Chem. Soc. 1915, **45**, 2177; abst. J. C. S. 1916, **110**, ii, 185. T. Hoffmann, Zts. Chem. Ind. Koll. 1912, 275; abst. C. A. 1912, **6**, 3235. N. Orloff, J. Russ. Phys. Chem. Soc. 1902, **34**, 52; abst. Chem. Centr. 1902, **73**, I, 1264; J. S. C. I. 1901, **20**, 943; 1902, **21**, 876.

6. A. Smith and W. Holmes, Zts. physik. Chem. 1903, **42**, 469; abst. Chem. Centr. 1903, **74**, I, 274; J. S. C. I. 1903, **22**, 322. P. Gaubert, Compt. rend. 1916, **162**, 554; abst. J. S. C. I. 1916, **35**, 600. L. Rotinjan, Zts. physik. Chem. 1908, **62**, 609. M. Raffo, Zts. Chem. Ind. Koll. 1908, **2**, 358. H. de Leeuw, J. C. S. 1913, **104**, 40; Beckmann, Chem. Zentr. 1913, **84**, II, 337. U. Panichi, Zts. Kryst. **54**, 393; abst. Chem. Zentr. 1915, **86**, I, 345.

Colloidal sulfur is produced in a variety of reactions in which sulfur is precipitated in aqueous solution. It is, perhaps best prepared by pouring a concentrated solution of sodium thiosulfate into strong, cooled sulfuric acid of sp. gr. 1.84. By adding water and neutralizing with sodium carbonate, a precipitate of sulfur is produced which is water-soluble.¹

The use of flowers of sulfur in treating the oidium disease of grape-vines is ascribed to the presence of traces of sulfuric and sulfurous acids always found in the commercial article, but to a less extent in roll sulfur.² This, however, has been controverted.³ Sulfur has been applied as a fertilizer,⁴ but the results obtained are contradictory, and its value is doubtful.

The heat of combustion of sulfur, according to J. Thomsen⁵ is, rhombic + O₂ = SO₂ + 71,080 gm. cal.; monoclinic + O₂ = SO₂ + 71,720 gm. cal. Berthelot gives 69,260 gm. cal. for rhombic S.⁶ On boiling sulfur with water, hydrogen sulfide is slowly evolved and sulfuric acid formed.⁷

Sulfur is soluble in a number of solvents, the most important

1. M. Raffo, Zts. Chem. Ind. Koll. 1908, **2**, 358; abst. J. S. C. I. 1908, **27**, 747. Thomsen Chemical Co., D. R. P. 273761. F. Imbert, F. P. 459534. P. Kulisch, Zts. ang. Chem. 1914, **27**, II, 415. C. Apostolo, Ann. Chim. anal. 1914, i, 124. L. Sarason, D. R. P. 216824, 216825, 262467. J. Meyer, Ber. 1913, **46**, 3089. Lumiere and Seyewetz, Bull. Soc. Franc. Phot. 1912, 375. Chem. Fabrik. von Heyden, D. R. P. 167664, 201371. Himmelbauer, Chem. Centr. 1909, **80**, II, 790. S. Oden, Zts. Chem. Ind. Koll. 1911, **8**, 186. Weimarn, Chem. Ind. 1911, **34**, 398. M. Raffo and J. Mancini, Zts. Chem. Ind. Koll. 1908, **2**, 358; 1911, **9**, 58; abst. C. A. 1912, **6**, 319. V. Vermorel and E. Dantony, Compt. rend. 1911, **153**, 194. C. Kelber and A. Schwarz, D. R. P. 245621.
2. R. Marcille, Chem. Ztg. Rep. 1911, **34**, 426. O. Rössler, Archiv. Pharm. 1887, 845. W. Zänker and E. Fäber, Färber Ztg. 1914, **25**, 343, 361; abst. Chem. Ztg. Rep. 1915, **39**, 110; J. S. C. I. 1915, **34**, 659. Chem. Zentr. 1913, **84**, II, 907; 1914, **85**, II, 1219. G. Rupprecht, D. R. P. 290240. N. Leonard, Analyst, 1901, **26**, 319; abst. J. S. C. I. 1902, **21**, 135.
3. E. Molz, Zts. ang. Chem. 1913, **26**, I, 534; abst. C. A. 1914, **8**, 196.
4. V. Sabaschnikoff, Russ. J. exper. Agric. 1912, 821; abst. Bied. Centr. 1914, **43**, 282; J. S. C. I. 1914, **33**, 1101. F. De Castella, J. Dept. Agric. Victoria, 1914, **12**, 289; abst. Pharm. J. 1914, 67; J. S. C. I. 1914, **33**, 1101. See also J. S. C. I. 1913, **32**, 69; 1914, **33**, 975. A. Demolon, Compt. rend. 1912, **155**, 524; **156**, 725. W. Thalau, Vers. Stat. 1913, 161; Zts. ang. Chem. 1913, **26**, II, 601. W. Thörner, Zts. ang. Chem. 1916, **29**, I, 233. J. Vogel, Chem. Zentr. 1914, **85**, I, 1212. T. Pfeiffer and E. Blanck, Zts. ang. Chem. 1914, **27**, II, 298. See J. S. C. I. 1915, **34**, 294, 1106. G. Bosinelli, J. S. C. I. 1915, **34**, 1064. H. Lint, J. Ind. Eng. Chem. 1914, **6**, 747.
5. Ber. 1880, **13**, 959; Jahr. Chem. 1880, **33**, 16.
6. M. Berthelot, Compt. rend. 1880, **90**, 1449.
7. C. Cross and A. Higgin, J. C. S. 1879, **35**, 241. Cf. A. Colson, Bull. Soc. Chim. 1880, (2), **34**, 66; J. Böhm, Jahr. Chem. 1882, **35**, 225. A. Smits, Zts. physik. Chem. 1913, **83**, 221; H. de Leeuw, Zts. physik. Chem. 1913, **83**, 245.

being carbon disulfide, carbon tetrachloride, sulfur chloride, petroleum and turpentine, although special solvents have been described.¹ It dissolves in hot concentrated sulfuric acid, forming sulfur dioxide, and in alkalis and milk of lime on heating, forming polysulfides and thiosulfates.²

Determination of Sulfur. The determination of sulfur in crude and refined brimstone, pyrites, spent-oxide, and in manufactured materials such as vulcanized rubber, asphalt, etc., is a matter of considerable importance, and in some cases one of difficulty.

Brimstone. The chief difficulty in this case is obtaining a representative sample. In the case of coarse sulfur, G. Lunge recommends taking 100 gm. of a crushed sample for the estimation of moisture, the crushing being done rapidly and only a coarse powder being aimed at. In large consignments it is recommended to sample in the same manner as pyrites, quartering in the car to 16 oz. sample, and breaking up all lumps during quartering.

The principal *impurities* in brimstone are: moisture, ash, arsenic (in the forms of arsenious oxide and sulfide, and rarely calcium and ferric arsenites), organic and bituminous matter, and selenium in Japanese sulfur.

Moisture is estimated by spreading about 20 gm. thinly on a watch-glass and drying for three days in a good sulfuric acid desiccator, or by heating on a water bath for one hour, the percentage of water being calculated from the decrease in weight. If heating is used, it should not exceed 70°, and should be continued no longer than necessary. This determination is of especial importance, as the percentage of sulfur is only indirectly

1. Chem. Fabrik von Heyden Akt. Ges., D. R. P. 284410. A. Vandenberghe (Belg. P. 136450, 1898) uses petroleum to extract sulfur from material containing the same.

2. For additional information consult: J. Smythe and W. Wardlow, Proc. Durham Phil. Soc. 1913-1914, **5**, 187; abst. J. C. S. 1915, **108**, ii, 335; J. S. C. I. 1915, **34**, 797. G. Brown, Amer. J. Sci. 1916, **42**, 132; abst. J. S. C. I. 1916, **35**, 926. L. Guitteau, Compt. rend. 1916, **163**, 390; abst. J. S. C. I. 1916, **35**, 1217. R. von Hasslinger, Monatsh. 1903, **24**, 729. A. Edinger and J. Ekeley, Ber. 1902, **35**, 96; abst. J. S. C. I. 1902, **21**, 285. B. Heinze, Chem. Centr. 1906, **77**, II, 699; 1907, **78**, II, 270; 1913, **84**, I, 2173. J. Dobbie and J. Fox, Proc. Roy. Soc. 1919, **95-A**, 484; abst. C. A. 1919, **13**, 1965. Solubility of sulfur in various solvents, R. Innes, J. Soc. Leather Trades Chem. 1919, **3**, 126; abst. J. S. C. I. 1919, **38**, 955-A; C. A. 1920, **14**, 475.

determined in the customary method of procedure.

Sulfur is determined by a variety of methods. (1) *Volatilization*. H. Fresenius and P. Beck¹ heat 10 gm. of sulfur to a little above 200° to volatilize the sulfur, weigh the residue, and incinerate. In this way the bituminous matter and ash is found. M. Levi² finds this method to give satisfactory results, but he recommends the oxidation method described below. (2) *Solution*. The sulfur is extracted by a solvent such as carbon disulfide. About 1 gm. is weighed into a tared Gooch crucible and extracted with CS₂ in a Wiley extractor, the soluble part being dried at 100° to constant weight. If tarry matter is present this method cannot be used. F. Carpenter³ found that only part of the sulfur could be extracted by CS₂ from Mexican sulfur, which contains gypsum. The loss of water of crystallization of the latter also precluded the determination by loss on ignition. In this case 2 gm. of material is weighed into a 250-cc. beaker, boiled for 10 minutes with dilute HCl, filtered, dried and weighed. The residue is sulfur and insoluble matter, from which the former can be extracted with CS₂.

I. Ceruti⁴ extracts the sulfur with aniline at 120°–130°. Methods for the extraction of sulfur by CS₂ have been described by H. Macagno,⁵ G. Pfeiffer⁶ and G. Lunge.⁷ The latter recommends the following process: The sample is shaken with exactly four times the quantity of pure CS₂, filtered, and the density determined at 15°. From this, the sulfur is estimated by means of tables given in the original.⁸ (3) *Oxidation*. M. Levi⁹ weighs 0.2 gm. sulfur into a 100 cc. conical flask, fitted by means of a ground glass joint to a reflux condenser. The flask is held in an inclined position immersed in cold water, and 10 cc. fuming nitric acid (sp. gr. 1.52) and 5 drops of bromine are introduced successively through the reflux. The flask is shaken occasionally till

1. Zts. anal. Chem. 1903, **42**, 21.

2. Annali Chim. appl. 1915, **1**, 9; abst. J. S. C. I. 1915, **34**, 282.

3. F. Carpenter, J. S. C. I. 1902, **21**, 832.

4. Boll. chim. farm. 1904, **43**, 421; abst. Chem. Centr. 1904, **75**, 1, 615.

5. Chem. News, 1881, **43**, 192.

6. Zts. anorg. Chem. 1897, **15**, 194.

7. "Chem. Technische Untersuchungsmethoden," **1**, 240.

8. W. Smith, J. Ind. Eng. Chem. 1915, **7**, 849. T. Reed, Chem. Ztg. Rep. 1897, **21**, 252. P. Klason and H. Melquist, Arkiv. Kgm. Min. Geol. 1911, **4**, No. 18, 1; abst. Chem. Ztg. 1911, **35**, 1345; J. C. S. 1912, **102**, ii, 201; Zts. ang. Chem. 1912, **25**, 514.

9. Annali Chim. appl. 1915, **1**, 9; abst. J. S. C. I. 1915, **34**, 282.

most of the sulfur and bromine are dissolved, when a further 5 cc. of nitric acid are added, and after heating half an hour on the water bath the flask is again immersed in cold water, the solution diluted with 50 cc. of cold water introduced in small portions through the reflux and the sulfur estimated by precipitation with barium chloride as usual. With low-grade sulfur the determination should be made with the sulfur separated from the original sample with CS_2 . A. Myhill¹ points out that in the method of extraction with CS_2 errors may arise from solvent left in the sulfur by the reaction: $\text{CS}_2 + \text{O}_2 = \text{CO}_2 + 2\text{S}$.

Chlorides. 20 gm. of the finely powdered dried sulfur are boiled in a 500 cc. beaker with 300–400 cc. distilled water until the solution is reduced to about 100 cc. The extract is then filtered, the residue washed, and filtrate and washings acidified with dilute nitric acid. The liquid is then titrated with $N/100$ AgNO_3 solution, using K_2CrO_4 as indicator, and the percentage of chlorine calculated as NaCl .

Arsenic. Ten gm. of finely ground sulfur is digested for 1 hr. with 50 cc. distilled water on the water bath, 10 cc. ammonia being added (10%). The solution is filtered, 10 cc. arsenic-free HNO_3 added to the filtrate, and the liquid evaporated to from 3–5 cc. Two cc. arsenic-free sulfuric acid are then added, and the mixture cautiously heated until white fumes are evolved. After cooling, a further 2 cc. of water are added, and the mixture again evaporated until white fumes are evolved. The liquid is then diluted to a concentration of about 20% H_2SO_4 , a little zinc added, and the Gutzeit test applied in the usual manner.

Selenium. 500 gm. sulfur are extracted with chloroform on an electrically heated water bath in a large Soxhlet extractor, or several smaller ones arranged side by side. The thimbles of the extractors are recharged with sulfur at intervals, and it has been found that when the sample of sulfur is 60-mesh or finer, the extraction is complete in about 6 hours. The residue is transferred to a porcelain crucible, 20 cc. nitric acid added, and the mixture evaporated to dryness on a water bath. The mass is treated with 100 cc. conc. HCl , the nitric acid boiled off, filtered through a Gooch crucible, and the residue washed with conc. HCl . 10 cc. conc. stannous chloride solution are then added,

1. Gas World; abst. Am. Gaslight J. **99**, 253; C. A. 1914, **8**, 234.

and the liquid allowed to stand 24 hours in the dark. The precipitated selenium is then Gooch filtered, and washed with HCl. The precipitate is re-dissolved in HNO_3 , and the solution evaporated to dryness. 100 cc. conc. HCl are then added, and the mass heated until free from HNO_3 . The liquid is then diluted, and treated with SO_2 gas. The development of a red color at this stage confirms the presence of selenium, which may thus be detected to a dilution of 0.0005%.

Ash. 25 gm. of the finely ground sample are weighed in a tared porcelain crucible, lighted, and carefully incinerated. The crucible is then heated over a flame, at first gently, and later more strongly. After cooling in a desiccator, and reweighing, the percentage of ash is calculated from the increase in weight.

Residue. About 25 gm. of the finely ground sample are weighed into a dried, tared Soxhlet thimble, and chloroform-extracted in a Soxhlet apparatus for 10 hours. The thimble and contents are then dried at 100° , cooled and weighed. The percentage of insoluble matter is then calculated from the increase in weight of the thimble, and the percentage of "residue" obtained by subtracting the ash percentage from the insoluble matter percentage. The "residue" is the "chloroform-insoluble," minus ash.

For the estimation of arsenic, see H. Schäppi,¹ F. Steel.²

The *Analysis of Spent Oxide* has been critically discussed by V. Hottenroth and others.³ In the extraction with carbon disulfide, substances other than sulfur are dissolved, which are not completely removed by washing the sulfur with ether. Wentzel recommends carbon tetrachloride as the extraction liquid, whereas the other two authors consider that the sulfur should be oxidized to sulfuric acid by fusion with sodium carbonate and potassium nitrate, and the sulfate precipitated with barium chloride. J. Marsden⁴ removes impurities from the sulfur left after the evaporation of the CS_2 used for extraction by treating it with concentrated sulfuric acid. 5 gm. of oxide are used for the first

1. Chem. Ind. 1881, **4**, 409.

2. Chem. News, 1902, **86**, 135. H. Hager, Pharm. Centralh. 1884, **26**, 263, 443. J. Brand, Chem. Zentr. 1908, **79**, I, 762.

3. V. Hottenroth, Wentzel, E. Wolf, H. Drehschmidt and Wirts, Ver. deutsch. Gaswerke A. G., Zts. ang. Chem. 1918, **31**, 127; abst. J. S. C. I. 1918, **37**, 413-A; C. A. 1918, **12**, 2430.

4. J. Gaslighting, 1914, **127**, 335; abst. J. S. C. I. 1914, **33**, 909.

extraction, and the residue evaporated in a tared 250 cc. flask, is heated on a steam bath with 10-20 cc. conc. sulfuric acid for 4 hours. 200 cc. distilled water are added, and the sulfur filtered off. The sulfur is washed free from acid, re-extracted with CS_2 , and the residue weighed. The difference in weighings gives the amount of organic matter present. Zulkowsky's method, which can also be used for pyrites, is described under the latter. An improvement of the method is to pass the gases, not through a solution of hypobromite, but through hydrogen peroxide, and to titrate the sulfuric acid formed by standard alkali, allowance being made for the acidity of the peroxide. The reaction is $\text{H}_2\text{O}_2 + \text{SO}_2 = \text{H}_2\text{SO}_4$.¹ C. Somerville² burns the spent oxide in a stream of oxygen and absorbs the SO_2 in caustic soda. The solution is oxidized with H_2O_2 and precipitated with barium chloride. E. Espenhahn³ heats 0.4-0.7 gm. of the sample previously finely powdered and washed, with 4 gm. of reduced iron in a hard-glass crucible, 30 mm. long and 10 mm. diam., keeping for 7 to 10 minutes at a dull red heat, the sulfur being converted into ferrous sulfide. The mass is cooled in a current of CO_2 , decomposed in a conical flask with strong hydrochloric acid, and the H_2S evolved passed into $N/10$ iodine and titrated in the usual way. The CS_2 extract of the spent-oxide gives the sulfur and tar; the latter is thus found by difference. The total sulfur, including that as sulfates and thiocyanates, is found on the unwashed sample. C. Davis and J. Foucar⁴ estimate sulfur in spent oxide as follows: 1 gm. of finely divided material (50 mesh) is dried on a water-bath for an hour, and transferred to a 250 cc. flask; 1.5 gm. sodium cyanide and 50 cc. absolute alcohol added, and the contents boiled under a reflux for two hours. The alcohol is distilled off, 100 cc. hot water added, and the solution transferred to a 250 cc. flask, the volume being made up in the cold. 25 cc. of this solution are taken, 75 cc. water and 5 cc. saturated iron alum solution added, and the mixture heated with constant stirring to 95° . It is filtered into a 750 cc. beaker and washed free from thiocyanate. When cool, 5 cc. nitric acid

1. K. Zulkowsky, *Dingl. Poly.* 1881, **241**, 52.

2. J. Gaslighting, 1914, 241; abst. C. A. 1914, **8**, 3498. See also C. A. 1911, **5**, 372; 1912, **6**, 676.

3. J. S. C. I. 1916, **35**, 292.

4. J. S. C. I. 1912, **31**, 100; abst. Chem. Zentr. 1912, **83**, I, 1735.

are added, the solution made up to 500 cc. with water, and titrated with $N/20$ AgNO_3 solution until the red color disappears. Other methods are those of M. Dennstedt and F. Hassler,¹ O. Pfeiffer,² and other investigators.³

To determine sulfur in asphalt, bitumen, etc., H. Schillbach⁴ mixes the material with excess of barium peroxide and ignites. The ash is washed with hydrochloric acid and the residue of BaSO_4 weighed. A. Hutin⁵ extracts free sulfur from commercial antimony sulfide by acetone, the extraction requiring 6 to 8 hours.

For the determination of sulfur in gunpowder, G. Petersen⁶ boils with alkali; the solution of sulfide is treated with hydrogen peroxide, warmed, acidified with HCl , and precipitated with BaCl_2 . For the estimation of sulfur in petroleum, D. Lohmann⁷ burns the oil under pressure in oxygen in a Mahler's bomb. The gases are passed into sodium carbonate solution, and the sulfate estimated as usual.

The estimation of sulfur in pyrites is usually effected by oxidation to sulfuric acid. As oxidizing agents there have been proposed aqua regia,⁸ hydrochloric acid and bromine,⁸ nitric acid and bromine,⁹ fusion with sodium carbonate and potassium nitrate, or sodium peroxide.¹⁰ Heating with sodium carbonate and zinc oxide has been recommended,¹¹ and manganese dioxide and magnesia,¹² as well as treatment with a solution of bromine

1. Zts. ang. Chem. 1905, **18**, 1563, 1903; 1906, **19**, 1668.

2. J. Gasbeluecht. 1905, **48**, 977; abst. Jahr. Chem. 1905-1908, I, 1536.

3. W. Diamond, J. S. C. I. 1908, **37**, 336-T; Gas J. 1919, **145**, 24; abst. C. A. 1919, **13**, 782.

4. Zts. ang. Chem. 1903, **16**, 1080; abst. J. S. C. I. 1903, **22**, 1309. H. Upton, J. Ind. Eng. Chem. 1918, **10**, 518. H. Stevens, Analyst, 1918, **43**, 377.

5. Ann. Chim. Analyt. 1916, **21**, 32; abst. J. S. C. I. 1916, **35**, 307.

6. Chem. Ztg. Rep. 1902, **26**, 355; Oversigt over Videnskabernes Selskabs Forhandlinger, 1902, **5**, 191; abst. J. S. C. I. 1903, **22**, 112.

7. Chem. Ztg. 1911, **35**, 1119; abst. J. S. C. I. 1911, **30**, 1244.

8. M. Lemaire, Zts. ang. Chem. 1903, **16**, 541; abst. J. S. C. I. 1903, **22**, 822. A. Smoot, Eng. Min. J. 1912, **94**, 412; abst. J. S. C. I. 1912, **31**, 918.

9. T. Craig, Chem. News, 1917, **115**, 253, 265; abst. J. S. C. I. 1917, **36**, 709.

10. Z. Karaoglanow and P. Dimitrow, Zts. anal. Chem. 1917, **56**, 561; abst. J. S. C. I. 1918, **37**, 204-A. H. Moore, J. Ind. Eng. Chem. 1916, **8**, 26; abst. J. S. C. I. 1916, **35**, 535; J. Ind. Chem. 1919, **11**, 45; abst. J. S. C. I. 1919, **38**, 171-A.

11. L. Sznajder, Chem. Ztg. 1913, **37**, 1107; abst. J. S. C. I. 1913, **32**, 941.

12. A. Reitlinger, J. Russ. Phys. Chem. Soc. 1902, **34**, 457; abst. Chem. Centr. 1902, **73**, II, 610; J. S. C. I. 1902, **21**, 1298.

in carbon tetrachloride.¹ The estimations may be made by gravimetric or volumetric methods. For further details see the section on Pyrites (pages 1043-1056).

Pyrites. The pure mineral pyrites is a disulfide of iron, FeS_2 , crystallizing in the forms of the cube and the pyritohedron, the former being often striated on the faces, the striae of one face being at right angles to those of the adjacent faces. It also occurs massive, in nodules which usually show a radiating structure, in finely disseminated crystals or particles,² and in combined forms. Commercial pyrites is usually mixed with gangue or other sulfides. The color is pale yellow to bronze, with metallic luster; the fracture conchoidal and irregular; the hardness 6 to $6\frac{1}{2}$, and the density 4.83 to 5.2. Pure FeS_2 contains 46.58% iron and 53.42% sulfur. Marcasite is a mineral of the same composition, but crystallizing in the rhombic system. It is lighter in color than that of pyrites, very easily undergoes oxidation in the air, producing ferrous sulfate and basic ferric sulfates,³ and has a sp. gr. 4.65-4.88.

Other varieties are pyrrhotite, Fe_7S_8 , and cuprous pyrites, the latter containing copper sulfide.⁴ This is golden yellow color, and in the pure state has the formula FeCuS_2 , containing 34.58% copper and 34.88% sulfur. Cupreous pyrites used in the manufacture of sulfuric acid, however, rarely contain more than 4% Cu.

The calorific value of pyrites has been approximately determined as 4957 gm. cal. per. gm. burning to $\text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \text{ aq.}$, or 2915 gm. cal. burning to $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_2$, in each case per gm. S. The latter values refer to 1 gm. pyrites, and is 1557 gm. cal. In all cases the pyrites is assumed to contain 53.2% S.⁵

Although the use of pyrites as a substitute for brimstone in the manufacture of sulfuric acid was patented by Hill in England as far back as 1818, its use on an extensive scale was first begun by his countryman, T. Farmer, in 1839. Pyrites has almost com-

1. W. Allen and H. Bishop, Eighth Intl. Cong. Appl. Chem. 1912, I, **1**, 33; abst. J. S. C. I. 1912, **31**, 919.

2. B. Doss, Chem. Ztg. 1912, **36**, 540.

3. P. Truchot, "Les Pyrites, Pyrites de Fer, Pyrites de Cuivre," Paris, 1907. A. Brown, Chem. News, 1895, **71**, 139. Stokes, Bull. 186, U. S. Geol. Surv. 1901. Oknow, Metallurgie, **8**, 539.

4. E. Sjöstedt, J. A. C. S. 1904, **26**, 305-R. B. Doss, Zts. prakt. Geol. 1913, **20**, 478; abst. Chem. Zentr. 1913, **84**, I, 737. T. Drakeley, J. C. S. 1916, **109**, 723. See Chem. News, 1916, **114**, 34.

5. E. Sommeijer, J. A. C. S. 1904, **26**, 555.

pletely supplanted brimstone in England, France and Germany. The question of the relative advantages of pyrites and brimstone in the manufacture of sulfuric acid has been summed up by G. Lunge¹ as follows: 'The advantages of brimstone are a somewhat higher yield of acid,—rather lower cost of plant, and above all, a greater purity of the acid. The advantages of pyrites are its greater cheapness—in most cases pyrites sulfur costs only half as much as brimstone, and the value of the copper in the pyrites cinder. Brimstone burner-gas also contains more SO₂ than that from pyrites. For the production of sulfur dioxide and sulfites for bleaching paper-pulp, sulfur burners are easier to work and there is less loss of sulfur. Since the Louisiana deposits have been exploited the use of brimstone in America has steadily increased.

Norwegian pyrites, containing about 40% S, and Spanish and Portuguese pyrites, containing about 49% S, are the usual varieties employed in the manufacture of acid, the former being nearly free from copper, while the latter contains 3%–4% copper. Belgian pyrites (45% S), French pyrites (45% S) and Italian pyrites (49% S with much arsenic), are used locally. Important deposits are also present in Russia, Canada and America.

The pyrites present in coal is unsuitable for acid manufacture on account of the tarry matter given off on roasting.

The weights of pyrites, in 1000 tons, consumed in different countries is shown in the following table.

| Year | America | England | France | Russia | Germany |
|------|---------|---------|--------|--------|---------|
| 1900 | 536 | 753 | 397 | ... | 627 |
| 1902 | 645 | 620 | 423 | ... | 645 |
| 1904 | 620 | 753 | 426 | ... | 678 |
| 1906 | 858 | 770 | 589 | ... | 776 |
| 1908 | 890 | 777 | 592 | ... | 878 |
| 1910 | 1007 | 810 | ... | ... | 1008 |
| 1912 | ... | ... | ... | 256 | 916 |
| 1915 | 1359 | ... | ... | ... | ... |

The production of pyrites in 1915 was 394,124 tons, the consumption 1,358,768 tons. The production of pyrites in Great Britain and Ireland in long tons of 2250 pounds, was for the

1. "Sulfuric acid and Alkali," 4th Ed. 560.

period 1910 to 1914, amounts as follows:

| | | | |
|------|-------------|------|-------------|
| 1910 | 9,380 tons | 1913 | 11,427 tons |
| 1911 | 10,114 tons | 1914 | 11,654 tons |
| 1912 | 10,552 tons | | |

The importation into Great Britain was 810,000 tons in 1910, and 849,921 tons in 1911.

The production and importation of pyrites in Germany was as follows:

| | Production | Importation (Less Exports) |
|------|------------|-------------------------------|
| 1911 | 217,459 | 851,204 |
| 1912 | 220,000 | 1,018,840 |
| 1913 | | 1,023,952 |

The productions in Austria-Hungary were:

| | Produced | Imported | Exported |
|------|----------|----------|----------|
| 1910 | 92,464 | | |
| 1911 | 100,000 | 150,000 | |
| 1912 | | 186,090 | 5,081 |
| 1913 | | 130,526 | 3,885 |

In 1910 France produced 250,000 tons, and in 1911 240,000 tons. In Russia the production in 1910 was 50,000 tons, and in 1912 130,000 tons. The imports in 1911 and 1912 were 115,000 and 145,000 tons, respectively.

Recent production of pyrites in Spain and Portugal is given as follows: The Rio Tinto Co. produced 2,406,969 tons in 1912, of which 698,399 tons were exported. In 1912, 2,080,000 tons of pyrites were exported from Huelva. In 1913, 2,733,000 tons were exported, of which 960,937 tons went to Germany and Holland, 668,680 tons to the United States, 512,487 tons to Great Britain, 353,455 tons to France, Tunis and Algiers, 89,995 tons to Belgium, 30,622 tons to Russia, 27,518 tons to Austria, and 24,895 tons to Italy. In 1913 Spain exported 2,903,554 tons, producing 730,568 tons iron pyrites, 2,000 tons copper pyrites, and 1,464,349 tons cupreous pyrites in 1915.¹

In 1911 Italy produced 170,000 tons, in 1913 292,077 tons non-cupreous and 28,973 tons cupreous pyrites; in 1913, 292,077 tons non-cupreous and 25,257 tons cupreous pyrites. The importation in 1911 was 115,000 tons.²

In the United States³ the production of pyrites in 1912 was

1. See also J. S. C. I. 1919, **38**, 248-R. Min. World, Aug. 1, 1908; abst. J. S. C. I. 1908, **27**, 855.

2. J. Sebelien, Chem. Ztg. 1914, **38**, 1119. O. Falkenberg, Zts. prakt. Geol. 1914, **22**, 105; abst. C. A. 1915, **9**, 1733.

3. U. S. Min. Res. 1914, II, 140; 1918, II, 357; abst. C. A. 1920, **14**, 451. P. Hopkins, Bull. Amer. Inst. Min. Eng. 1916, 1361; abst. C. A. 1916,

350,928 tons, in 1913 it was 341,338 tons, in 1914 336,662 tons, and in 1915, 394,124 tons. The imports in 1915 were 964,634 tons.

The production of pyrites in Japan was 30,000 tons in 1910 and 9,000 tons in 1911.

Analysis of Pyrites. A great number of methods have been proposed for the analysis of pyrites. The sampling of the consignment must, of course, first be carefully made, the final sample being coarsely ground and kept in a stoppered bottle.

Moisture is estimated by drying at 105°, and the other results are calculated on the dry pyrites. Sulfur is estimated by oxidizing the powdered pyrites by aqua regia, and precipitation with barium chloride.

Great Britain possesses several deposits of pyrites, none of great importance. The mineral occurs in Cornwall, Devonshire, Cleveland (North Yorkshire), Ireland (County Wicklow), Wales (Cae Coch Mine), and a few other localities. These pyrites have now gone almost entirely out of use.

The most important German source is the bed at Meggen, Westphalia, the analysis of which is as follows:

| | a | b | Average |
|--------------|-------|---------------|------------|
| Gangue..... | 12.02 | 12.96 | 12.0 |
| Sulfur..... | 41.94 | 43.42 | 40-43 |
| Iron..... | 34.92 | 35.56 | 35 |
| Zinc..... | 7.56 | 5.81 | 7 |
| Lead..... | 0.38 | not estimated | 0.3-0.5 |
| Arsenic..... | trace | 0.05 | trace-0.05 |
| Total..... | 97.32 | 97.80 | |

The smaller beds of pyrites exist near Goslar, near Schwelm (Westphalia), and near Merzdorf (Silesia). A great drawback to the German ores is the presence of zinc, in consequence of which sulfur is left in the burnt ore in the form of sulfate.

Large beds of pyrites occur in Austria-Hungary at Chemnitz and Schmoelnitz in Hungary, in Styria and Tyrol. The former contains 47%–48% sulfur, 39%–40% iron, 0.58% copper, 1.5%–

10, 2337. Separation of pyrites from coal is described by C. Binks, E. P. 2998, 1864. Magnetic concentration by J. Bonardi, Chem. Met. Eng. 1919, **20**, 266; C. A. 1919, **13**, 1745. For the manufacture of pyrites in briquettes, see U. S. P. 53742, 135512, 252287, 421878, 485840, 687085, 733682, 757531, 760561, 804690, 804691, 804692, 804785, 894464, 894799, 899219, 901599, 1008847, 1013614. E. P. 4580, 1904; 1639, 1908.

2% zinc, together with lead, silver (81 grains per ton), and gold (2.2 grains per ton). Schmoelnitz ore contains 44%–48% sulfur, 0.4%–0.6% copper, 2%–3% zinc. Pyrites containing 49% sulfur and 6% carbon occurs at Davidsthal, in Bohemia.

The pyrites found in Switzerland in the Canton of Wallis contains about 50% sulfur, but does not seem to have found industrial application. In Poland¹ pyrites occurs with blende, containing thallium.

Belgian pyrites are rich in sulfur, but have the drawback of being friable. The ore is used locally, or in the north of France. The percentages of sulfur vary from 35.5 to 50.0, a small amount of zinc being always present (0.22%–5.26%). The production is now very small.

In France the principal deposits are those of the Rhon (Chessy and Sain-Bel), and of the South (Gard and Ardèche). The former are more important, the ore being mostly non-cupreous, although a vein with 4%–5% copper occurs. The second beds are more numerous but of less importance.² The Chessy ore contains 47%–48% of sulfur; Sain-Bel, about 47% (non-cupreous; cupreous 38%), Saint-Julien 41%–44%, and Soyons 44%–49%.

Italy possesses several beds of pyrites, such as those in the province of Bergamo, in the Val d'Aosta, at Brosso, near Ivrea, and of very good quality in Sicily. Some pyrites are imported from Spain.³

Swedish pyrites, from Fahlun, contain from 43% to 48% sulfur, and occurs in large amounts, but transportation is difficult.

Norwegian pyrites form an important source, the richer ores, even those free from copper, being used on account of their free burning qualities, although they are difficult to break. The chief deposits are at Ytteroen, although other deposits occur near Drontheim and Bergen. The Norwegian ore contains very little arsenic.⁴

Pyrites occur in Russia,⁵ mostly in the Ural district, but at

1. J. Antipow, J. Russ. Phys. Chem. Soc. 1896, **28**, 384; abst. Wag. Jahr. 1897, **43**, 421.

2. A. Girard and H. Morin, Compt. rend. 1875, **81**, 190; Ann. Chim. Phys. 1876, (5), **7**, 229; abst. Jahr. Chem. 1875, **28**, 1198.

3. P. Candiani, Chem. Ind. 1895, **18**, 153. See Drinkwater, Analyst, 1885, **10**, 109; abst. J. S. C. I. 1885, **4**, 533.

4. J. Vogt, Zts. Elektrochem. 1903, **10**, 856; Fifth Intl. Cong. Appl. Chem. 1904, II, 90. See Chem. Ind. 1911, **34**, 755.

5. Chem. Trade J. 1911, **49**, 29; **50**, 71; Eng. Min. World, Oct. 14, 1911.

a distance from chemical industries. It roasts badly, giving much dust, and contains carbonaceous matter.

The most important deposits of pyrites occur in Spain and Portugal.¹ The ore has been worked only since 1855, although it was known to the Romans. All the beds occur in a narrow belt, running parallel to the Sierra Morena from the western frontier of Seville across the hilly country to the south through Portugal to the Atlantic Ocean. The pyrites occurs in large pockets, containing no visible gangue. The percentage of copper varies from 2.5 to 40, but ores containing more than 10% of copper occur only in small vertical zones in the larger masses, although immense quantities are present in the beds. The companies working the ore are mostly in French and British hands. The San Domingo mine lies in Portuguese territory; its ore, known as Mason's ore, is of very good quality and commands a better price than the others. The largest company is the Rio Tinto Co., supplying ore of very good quality, chiefly to British markets.

The following are analyses of average Spanish and Portuguese ores:

| Ores | Rio Tinto | | S. Domingo | | Tharsis | |
|--------------|-----------|------|------------|-------|---------|-------|
| Sulfur..... | 48.00 | 50.7 | 49.00 | 49.0 | 49.80 | 47.5 |
| Iron..... | 40.00 | 41.3 | 43.55 | 41.41 | 43.55 | 41.92 |
| Copper..... | 3.42 | 3.5 | 3.20 | 2.46 | 3.20 | 4.21 |
| Lead..... | 0.82 | | 0.93 | 0.98 | 0.93 | 1.52 |
| Zinc..... | trace | | 0.35 | 0.44 | 0.35 | 0.22 |
| Arsenic..... | 0.21 | | 0.47 | 0.55 | 0.47 | 0.38 |

Certain Spanish ores decrepitate badly in the burners, probably owing to their containing hydrated silicates. Large quantities of "leached ore" now come from Spain. These have been weathered and then washed with water to extract the copper, only 0.3%–0.5% being left in the ore. They contain 49%–50% sulfur, but make much dust on burning. Non-cupreous pyrites is also found in Spain, especially at the Aguas Teñidas mine, the

1. F. Schönnichen, *Dingl. Poly.* 1863, **167**, 448. G. Lunge and E. Bänziger, *Zts. ang. Chem.* 1896, **9**, 421; 1905, **18**, 759. K. Reusch, *Chem. Ztg.* 1906, **30**, 326.

ashes of which are considered especially suitable for iron-smelting.

The United States is very rich in pyrites, the principal mines at present worked being the following: New Hampshire, at the Milan mines, Coos County, where the ore is sorted into two grades, No. 1 being the best, although No. 2 is of good-burning quality.

| | No. 1 | No. 2 |
|--------------|-------|-------|
| Sulfur..... | 46.0 | 35.0 |
| Copper..... | 3.7 | 5.0 |
| Iron..... | 40.0 | 30.5 |
| Silica..... | 6.2 | 25.5 |
| Zinc..... | 4.0 | 8.0 |
| Arsenic..... | nil | nil |

In New York, pyrites occurs at St. Lawrence, Hendon County, containing 38.0% sulfur. In Virginia there are the Arminius Copper Mines Co. and Sulfur Mines Co., both in Louisa County. The ore contains 49.5% sulfur and 0.5% copper. Virginia was the largest producer in the United States in 1909. Pyrites is found at Pyriton, Alabama; in Georgia, in Illinois, Indiana, Massachusetts, Ohio, Pennsylvania, Wisconsin, and Gainesville, Ga.¹ It is stated that, roughly speaking, about half the acid made in the United States is from pyrites and the balance from brimstone.

There are two mines in Canada, the Albert mine and the Crown mine, the ore containing 40% sulfur. Both American and Canadian ores are therefore of lower quality as compared with European ore.

Pyrites occurs in Newfoundland,² South Australia³ and North Borneo.⁴

The value of pyrites in England is reckoned per "unit," or per cent. of sulfur per ton. This has been from 1/- in 1860 to 3d. in 1885, and has risen to 4d.-4½d. in 1911. An allowance is made for copper above a minimum percentage.

Pyrites is always carried in bulk, whether by rail or sea. A strong acid liquid may form if water is allowed access.⁵

The question of the proportional value of poor and rich ores

1. Ektel, U. S. Geol. Survey Bull. 213, 62. K. Stahl, Zts. ang. Chem. 1893, **6**, 54.

2. Anon., Eng. Min. J. 1892, 467.

3. C. Mepe, Mon. Sci. 1867, **9**, 411.

4. Chem. Ztg. 1909, **33**, 82.

5. H. Mastbaum, Chem. Ztg. 1912, **36**, 30; Chem. Trade J. **50**, 358.

is rendered difficult by the different costs of breaking and burning the ores. The percentage of sulfur left in the cinders is also the same in both cases, so that the available sulfur is not simply proportional to the percentages.

Volumetric Analysis of Pyrites. The method of titrating a solution containing a sulfate, such as is obtained by dissolving pyrites in aqua regia, has been used.¹ The solution is neutralized with sodium carbonate, boiled in a porcelain dish, and an excess of standard 4% barium chloride solution run in. A few drops of phenolphthalein are added and the excess of barium chloride precipitated by standard sodium carbonate solution, the end point being shown by the solution turning red. A similar process has been proposed for the estimation of sulfur in burnt pyrites.² This method, due to J. Watson, has been improved upon by G. Lunge³ as follows, and is said by him to give accurate results: 3.2 gm. of the finely powdered sample are mixed with 2.00 gm. of sodium bicarbonate of known titer, heated in a nickel crucible for 10-15 minutes with a small flame, and the heating continued for another 15 minutes with a strong flame. The mass should not be fused, the crucible should be covered, and the contents not stirred. The mass after cooling is transferred to a porcelain dish with water, adding the same volume of a neutral solution of sodium chloride to prevent oxide of iron passing through the filter. The filtered solution is titrated with standard acid and methyl orange. The difference between the original titer of the bicarbonate and this final titer gives the amount of sulfur, 1 cc. N acid giving 0.5% of sulfur. The method does not apply in presence of considerable quantities of zinc.

The amount of magnetic pyrites present may be determined by grinding the ore to a fineness of 60 mesh, spreading the powder on a sheet of glazed paper, applying a magnet, removing mechan-

1. R. Wildenstein, *Zts. anal. Chem.* 1862, **1**, 432. E. Teschemacher and J. Smith, *Chem. News*, 1871, **24**, 61, 66. See also N. Glendinning and A. Edger, *Chem. News*, 1871, **24**, 140. C. and J. Beringer, *Chem. News*, 1889, **59**, 41. H. Wilsing, *Chem. Ind.* 1886, **9**, 25. L. Andrews, *Amer. Chem. J.* 1889, **11**, 567; *abst. Chem. Ztg. Rep.* 1889, **13**, 39. M. Reuter, *Chem. Ztg.* 1898, 357. F. Marboutin and M. Moulinic, *Bull. Soc. Chim.* 1897, **17**, 950; *abst. Chem. Centr.* 1898, **69**, I, 218.

2. J. Watson, *J. S. C. I.* 1888, **7**, 305.

3. G. Lunge, *Zts. ang. Chem.* 1892, **5**, 447. "Technical Methods of Chem. Analysis," **1**, i, 298. C. Nitchie, *J. Ind. Eng. Chem.* 1912, **4**, 30. J. Peregrin, *Ann. Chim. Analyt.* 1917, **22**, 26; *abst. J. S. C. I.* 1917, **36**, 335.

ically adhering pyrites by gentle tapping, and brushing off the magnetic pyrites after putting on the keeper of the magnet.¹

For the estimation of copper, etc., in pyrites, reference may be made to a paper by J. Westmoreland.²

Gravimetric Analysis of Pyrites. In the gravimetric analysis of pyrites the following determinations may be made:

Sampling. Carload lots are sampled by taking $\frac{1}{4}$ shovelful from every wheelbarrow load (10 shovels to a barrow), which gives about a barrowful per carload. This is well mixed, and a sample of about 5-6 lbs. taken for the moisture. The remainder is quartered about five times to about 50 lbs. in the car, and is then sent to the laboratory. It is there quartered to about a 32 oz. bottle full. This is ground to pass 20 mesh, and quartered; ground to pass 40 mesh and quartered; ground to pass 80 mesh and quartered; ground to pass 100 mesh and quartered; ground to pass 200 mesh. The final sample at this point should be about 100 gm.

Moisture. The 5-6 lbs. sample from the first quartering in the car is weighed in a bottle on a large scale, emptied into a large tray, dried overnight at 100° in an electric bath, transferred to the bottle and reweighed, the loss being moisture. The moisture is also determined on the 200 mesh sample and the following results corrected for the moisture in the original sample.

Insoluble matter. About 0.5 gm. is accurately weighed into a 3" porcelain dish, carefully treated with 20 cc. nitric acid (1:1), covered with a watch glass and heated on a hot plate with the addition of a few crystals of KClO_3 until all sulfur is oxidized. If necessary, more nitric acid may be added. The solution is then twice evaporated to dryness with HCl , using 10 cc. each

1. B. Cone, J. A. C. S. 1896, **18**, 404.

2. J. S. C. I. 1886, **5**, 31, 277. See also N. Tarugi and G. Bianchi, Chem. Centr. 1906, **77**, II, 708. W. Lang and T. Allen, J. C. S. 1907, **91**, 1370. U. Borgi and T. Sotgia, C. A. 1916, **10**, 1308. See also Y. Nikaido, J. A. C. S. 1902, **24**, 774. B. Riegler, Zts. anal. Chem. 1902, **41**, 17. M. Mohnhaupt, Chem. Ztg. 1904, **28**, 1125. C. Blacher and V. Koerber, Chem. Ztg. 1905, **29**, 722. E. Martin, Mon. Sci. 1914, **80**, 86. J. Grossman, Chem. News, 1880, **41**, 114, 183. F. Telle, Chem. Centr. 1898, **69**, I, 218. M. Scholtz, Arch. Pharm. 1905, **243**, 667. W. Müller, Ber. 1902, **35**, 1587. W. Müller and K. Dürkes, Zts. anal. Chem. 1903, **42**, 477. F. Raschig, Zts. ang. Chem. 1903, **16**, 617, 818; 1906, **19**, 332. G. Knorre, Chem. Ind. 1905, **28**, 2. C. Friedheim and O. Nydegger, Zts. ang. Chem. 1907, **20**, 9. J. Nickel, Zts. ang. Chem. 1910, **23**, 1560. A. Zehetmayr, Zts. ang. Chem. 1910, **23**, 1359. V. Hassreidter and P. Van Zuylen, Chem. Centr. 1905, **76**, I, 1433.

time, in order to remove the HNO_3 and render the silica insoluble. The residue is then moistened with conc. HCl , 20 cc. 30 cc. water added, and the mass well stirred and filtered. The residue on the filter is washed until neutral, dried, ignited and weighed. It should be almost colorless and show no trace of red color due to iron.

Iron. The filtrate and washings from above are heated to boiling, a slight excess of ammonium hydroxide added, and the whole kept near the boiling point for 10 minutes. After allowing to stand in a warm place for some time, the precipitated ferric hydroxide is filtered, washed with the minimum amount of boiling water until sulfates are removed. The filtrate and washings may be used for the determination of sulfur. The precipitate is dissolved on the filter with a small quantity of hot, dilute HCl , well washed, and the solution and washings heated nearly to boiling. Slight excess of ammonium hydroxide is then added, and the iron re-precipitated and treated as before. The filtrate and washings from this second operation are made slightly acid with HCl , heated to boiling, and 10 cc. of 10% BaCl_2 slowly added. If any appreciable precipitate is obtained, it is filtered, washed and ignited with the main BaSO_4 precipitate subsequently obtained. The ferric hydroxide is washed, dried and ignited, and the percentage of iron calculated in the usual manner.

Copper. About 5 gm. finely ground pyrites are weighed into a large porcelain dish, and treated with conc. HNO_3 . After heating some time, conc. HCl is added, and the solution finally evaporated to dryness with excess of sulfuric acid to convert the bases into sulfates. Heating is continued until sulfuric acid fumes are freely evolved, in order to insure the removal of all nitric acid. The residue is then lixiviated with warm water, and the insoluble matter removed by filtration. The filtrate is heated to boiling, and the copper precipitated with $\text{N}/\text{Na}_2\text{S}_2\text{O}_3$ solution. The precipitate is filtered, washed with hot water, dried and ignited. The resulting copper oxide is then dissolved in nitric acid, and after the major portion of the free acid has been removed by evaporation, sodium carbonate is added to precipitate part of the copper and ensure that the solution is free from mineral acid. Acetic acid is then added until a clear solution is formed, and about 10 parts KI for every part of copper supposed to be present in

the solution. The solution is then titrated with $N/Na_2S_2O_3$ in the usual way, 1 cc. thiosulfate solution being equivalent to 0.006357 gm. Cu.

Sulfur. About 0.5 gm. of the fine sample is treated with 10 cc. of a mixture of 3 vols. nitric acid (sp. gr. 1.4) and 1 vol. fuming hydrochloric acid, both acids being free from sulfuric acid. As action diminishes, warm gently, care being taken to avoid spurting. The digestion may be carried out in a casserole covered with a watch-glass. If free sulfur separates, a little potassium chlorate may be added as an oxidizer. The liquid is evaporated to dryness on a steam bath, 5 cc. conc. HCl added, and the evaporation repeated, after which no odor of nitric acid should be noticeable. 1 cc. conc. HCl and 100 cc. hot water are then added.

The insoluble residue may consist of barium, calcium and lead sulfates, silica, etc., the sulfur content of which is unavailable for the manufacture of sulfuric acid and may be disregarded. If the total sulfur in the pyrites is to be estimated the residue should be fused, otherwise it may be disregarded and the filtration omitted. The volume of the solution being about 150-160 cc. it is heated to 70° and ammonium hydroxide (sp. gr. 0.90) added in excess (5 cc.). The temperature is maintained at 70° for 10 minutes, and the precipitate of ferric hydroxide filtered off and washed thoroughly with hot water. The precipitate may be re-dissolved in a small quantity of hydrochloric acid and re-precipitated.

The volume of the filtrate and washings being about 300-350 cc. a few drops of methyl orange are added and then fuming hydrochloric acid (sp. gr. 1.20) in 1 cc. excess. The solution is heated to boiling and a hot solution of 10% barium chloride added in small portions at a time with constant stirring until no further precipitation occurs. About 20 cc. should be more than sufficient for 0.5 gm. of the sample, and excess should be avoided.¹ The liquid is boiled for a few minutes after precipitation, and is allowed to stand forty minutes to settle. The clear liquid is decanted through a filter, and 100 cc. boiling water poured on the precipitate in the beaker, with stirring. After settling for two or

¹ For minute details for the precipitation of sulfuric acid by barium chloride, see E. Worden and J. Motion, J. S. C. I. 1905, **24**, 178.

three minutes the decantation is repeated. This washing by decantation is repeated three or four times, and the precipitate then washed on the filter until free from chlorides, when it is dried and ignited. The precipitate and paper may be burned together or separately. In the former case strong ignition in an inclined crucible is necessary to oxidize any BaS to BaSO₄. The precipitate should be quite white and should not firmly cake together.

Constants for calculation:

| | | | | |
|---|----------------------|--------|-----|----------|
| BaSO ₄ | Molecular weight.... | 233.46 | log | 2.36822 |
| S..... | Atomic weight..... | 32.06 | log | 1.50596 |
| To convert BaSO ₄ to S, add..... | | | log | 9.13797. |

The above directions for quantities of reagents must be followed exactly. All reagents must be free from sulfuric acid or sulfates.

In the determination of arsenic the following method may be used: 10 gm. of the fine sample are dissolved in a large beaker with nitric acid (sp. gr. 1.2) and transferred to a porcelain or platinum dish. 50 cc. sulfuric acid added, and the liquid evaporated until copious fumes of sulfuric acid are given off. The dish is cooled and 50 cc. water added, the evaporation being repeated until the excess of sulfuric acid is driven off and the ferric sulfate is so dry that it is readily transferred to a flask of about 500 cc. capacity. Add to the mass in the flask 15 gm. finely powdered ferrous sulfate, pour in 50 cc. strong hydrochloric acid and connect to a flask.

Heat the liquid gradually in the flask until it boils and continue the distillation, the arsenic acid in solution being reduced by the FeSO₄ and in presence of the HCl is distilled off as arsenous chloride. Remove the burner and heat the solution in the beaker to about 70°, passing a current of H₂S through it until it is completely saturated. Remove the excess of H₂S by a current of carbon dioxide and when the solution smells but faintly of H₂S, filter off the yellow precipitate of As₂S₃ in a Gooch crucible or counterpoised filter, wash with water, alcohol and finally with pure carbon disulfide. Dry at 100° and weigh as As₂S₃, which contains 60.93% As. The precipitate on the Gooch may also be dissolved in fuming nitric acid, filtered, evaporated to about 10 cc. and 5 cc. magnesia mixture added. Ammonia is then

added equal to half the volume of the solution, which is stirred vigorously from time to time, the liquid being kept cool in ice-water. It is allowed to stand for 12 hours, filtered, washed with NH_4NO_3 solution, dried at 103° for 30 minutes, ignited strongly for a few minutes and weighed as magnesium arsenate containing 68.30% As.

Numerous special methods have been proposed for the gravimetric analysis of pyrites. K. Zulkowski¹ burns the ore in a current of oxygen in a tube of hard-glass, quartz² or clear silica,³ in a boat followed by a pad of platinized asbestos or platinized quartz.⁴ The vapors of SO_2 and SO_3 are absorbed in bulbs containing caustic potash and bromine, or dry carbonate, afterwards treated with bromine. The sulfuric acid is determined as usual by precipitation, or by the method of F. Raschig⁵ by precipitation with benzidine and titration of the precipitate with caustic soda and phenolphthalein. Another method⁶ consists in heating the pyrites with iron or aluminium powder, and decomposing the sulfides with hydrochloric acid, the H_2S being absorbed in standard iodine solution.

Other constituents which may be estimated in pyrites are calcium carbonate (which retains 0.32% S for every per cent. CaCO_3 , in the form of CaSO_4 on burning),⁷ calcium sulfate, which gives off no sulfur on burning, lead,⁸ zinc,⁹ and copper,¹⁰ which form

1. Ber. oest. Chem. Ges. 1881, 2; abst. Wag. Jahr. 1881, **27**, 160. E. Lundin, Jern-Kontoretz-Annaler, 1883, 360; abst. Jahr. Chem. 1884, **37**, 1582.

2. A. Hezko, Zts. anal. Chem. 1911, **50**, 748; 1912, **51**, 1. P. Janasch, J. prakt. Chem. 1889, **148**, 237.

3. M. Dittrich, Zts. anorg. Chem. 1913, **83**, 27; abst. C. A. 1913, **7**, 3726.

4. M. Dennstedt and F. Hassler, Zts. ang. Chem. 1906, **19**, 1668. G. Lunge, Zts. ang. Chem. 1906, **19**, 1854.

5. See A. Hezko, Zts. anal. Chem. 1912, **51**, 1; abst. J. S. C. I. 1912, **31**, 227.

6. M. Groeger, Dingl. Poly. 1881, **241**, 53; abst. Wag. Jahr. 1881, **27**, 161. F. Treadwell, Ber. 1891, **24**, 1937, 2377. S. Blasberg, Zts. anal. Chem. 1887, **26**, 240. C. von Hohorst, Chimiste, **2**, 97; abst. C. A. 1911, **5**, 2051.

7. G. Lunge and C. Keane, Tech. Methods Chem. Analysis, **1**, 149. G. Lunge and A. Rittener, Zts. ang. Chem. 1906, **19**, 1849.

8. H. Koch, Chem. Ztg. 1908, **32**, 587.

9. G. Lunge and C. Keane, "Technical Methods of Chemical Analysis," **1**, 272. See also F. Giolitti and M. Marantonio, Rassegna Min. Met. Chim. 1911, 35; abst. Chem. Zentr. 1912, **83**, I, 1250; J. S. C. I. 1912, **31**, 393. F. Hawley, Eng. Min. J. 1918, **105**, 385; abst. C. A. 1919, **13**, 403. H. Rubricus, Chem. Ztg. 1915, **39**, 198. Z. Karaoglanow and P. and M. Dimtrow, Zts. anal. Chem. 1917, **56**, 561.

10. R. List, Zts. ang. Chem. 1903, **16**, 416. O. Heidenreich, Zts. anal. Chem. 1901, **40**, 15. W. Treadwell, Chem. Ztg. 1912, **36**, 961. J. West-

stable sulfates on roasting, arsenic,¹ selenium,² silica, which in the form of zeolites causes decrepitation on burning,³ and carbon.⁴

The estimation of sulfur in zinc blende⁵ may be made by⁶ dissolving the powdered blende in a mixture of hydrochloric acid

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and bromine, boiling off the excess of acid and precipitating with barium chloride.

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used in the manufacture of sulfuric acid are obtained, are chiefly the following:

- (1) Iron pyrites, usually containing copper.
- (2) Native sulfur, or brimstone, chiefly used in the manufacture of fuming sulfuric acid or oleum.
- (3) Zinc blende, copper mattes, and other sulfide ores
- (4) Spent-oxide (Fe_2O_3 with up to 60% free sulfur) obtained as a by-product in the purification of coal-gas.
- (5) Leblanc alkali-waste, containing calcium sulfide.

The major portion of the acid produced is probably made

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from pyrites, although the use of brimstone is rapidly increasing, especially in the United States. The acid made from blende or

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by the roasting of sulfide ores or mattes is really a by-product of metallurgical industry, and increasing in importance. The use

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For the manufacture of sulfur dioxide and sulfurous acid, the following English patents may be consulted: 2197, 1861; 113, 1084, 2275, 2565, 1862; 611, 967, 1776, 2203, 3044, 1863; 580, 1545, 1864; 729, 1385, 2100, 2350, 2535, 1865; 121, 1948, 2593, 3117, 3401, 1866; 1040, 1867; 270 1457, 2600, 3101, 1868; 469, 1575, 2756, 3756, 1869; 510, 2823, 2866, 1870; 79, 753, 972, 1920, 1923, 1928, 2381, 1871; 145, 794, 1540, 3461, 1872; 3760, 1873; 2708, 2884, 3087, 4153, 1874; 681, 2460, 2481, 2727, 3278, 1875; 15, 1103, 1773, 1782, 2285, 2737, 2950, 3094, 3593, 4048, 4624, 1876; 820, 2842, 3082, 1877; 215, 356, 1131, 1281, 2880, 4549, 4755, 5159, 1878; 189, 895,

from alkali-waste and its reconversion into sulfuric acid forms an integral part of the Leblanc alkali industry, and may be expected to decline with the latter, although the possibility of producing sodium sulfide directly from the sulfate by heating with carbon, and the direct decomposition of the sulfide with carbon dioxide has recently been investigated.

Sulfur dioxide is produced from all the above materials by roasting them at a more or less elevated temperature in a current of air, except in the case of alkali-waste, which must first be treated for recovery of sulfur by the Chance-Claus process (p. 1030). The combustion of brimstone, spent-oxide and pyrites, evolves sufficient heat to be self-supporting, but in the roasting of blende or mattes, additional heat must be supplied in special furnaces.

Proposals to utilize blast furnace gas from copper smelting have been made.¹

Sulfur Burners. The chief difficulty in burning brimstone 983, 3196, 3774, 4364, 1879; 1456, 2784, 1880; 1893, 2080, 2575, 3443, 3560, 4218, 4857, 1381; 120, 955, 1014, 1494, 1665, 1913, 3186, 3608, 3714, 5412, 1882; 1349, 2621, 3725, 4356, 5070, 5958, 5959, 5960, 1883; 603, 5930, 6982, 7977, 9761, 11655, 11866, 13045, 15393, 17106, 1884; 3049, 3761, 6405, 6626, 7355, 8838, 8912, 11178, 12261, 13950, 14364, 14780, 15988, 1885; 872, 5016, 5681, 6370, 7355, 7361, 10000, 13928, 14711, 14875, 15488, 1886; 3704, 8441, 10127, 10153, 10818, 10957, 14345-A, 17050, 1887; 1393, 2426, 3166, 4648, 5212, 15063, 15676, 15980, 1888; 4602, 6968, 12028, 1889; 13240, 15806, 21217, 1890; 2000, 4712, 5357, 7362, 9947, 9948, 16647, 19953, 1891; 2261, 2629, 6567, 14264, 19789, 20269, 1892; 2119, 2883, 3111, 4342, 5349, 9042, 11807, 20604, 1893; 2373, 4195, 1894; 199, 1322, 8374, 22037, 22038, 22039, 1895; 3906, 5184, 6096, 8064, 8072, 12643, 13844, 16312, 25133, 1896; 3795, 8335, 11151, 24121, 1897; 142, 7269, 11633, 15947, 15948, 17266, 1898; 4966; 7357, 8123, 24731, 24748, 1899; 817, 1216, 10317, 11687, 15134, 16253, 1900, 2368, 3327, 7725, 8088, 10351, 12349, 13302, 15250, 17580, 19902, 20077, 20566, 21546, 1901; 4892, 7119, 1902; 1755, 11549, 13454, 1903; 2655, 6898; 11437, 16353, 1904; 2861, 11300, 11986, 14409, 16931, 19839, 24238, 25371, 1905; 3994, 16912, 19130, 21672, 22166, 24826, 25574, 1906; 974, 2789, 3435, 12213, 17125, 19973, 23901, 26052, 27017, 27019, 27020, 1907; 273, 701, 1639, 1695, 1761, 2414, 2971, 7429, 12317, 14707, 21759, 23497, 25535, 26152, 1908; 9145, 13081, 13291, 19776, 20494, 20504, 22672, 1909; 8006, 9869, 12137, 12138, 20048, 20186, 21214, 28126, 1910; 17157, 21996, 27451, 1911; 2140, 8218, 10810, 12027, 19600, 26099, 1912; 103689, 106585, 107589, 108688.

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is that the material becomes liquid, and special furnaces are required in order to retain the liquid and ensure that it is constantly brought in contact with a sufficient supply of air. If the supply of air is deficient, sublimation of sulfur occurs.

Sulfur burners for acid works are mainly of two kinds: (1) hand operated, (2) mechanical. The burners used in most British oleum works are hand operated, since the labor is exceedingly light, and may be carried out with a minimum number of operatives. In the United States the mechanical burner is favored.

In the hand operated burner the solid sulfur is thrown on a shelf in the furnace, where it melts and burns. The hot gases pass back underneath the shelf in order to conserve its heat. The layer of melted sulfur is shallow, and an adequate supply of air is ensured to prevent sublimation.

A large number of special types of sulfur burners have been described, but few appear to have been in practical use, the simple burner just described being commonly employed.¹ Among the suggestions which have been put forward are mechanical

1. H. Blumenberg, U. S. P. 734397, 788512; abst. J. S. C. I. 1903, **22**, 950. C. Brackelsberg, E. P. 27451, 1911. L. Brochon, F. P. 355252; abst. J. S. C. I. 1905, **24**, 1171. C. Clark, U. S. P. 952098, 952099, 952100; abst. C. A. 1910, **4**, 1527. F. Coombs, U. S. P. 1147376, 1915; abst. J. S. C. I. 1915, **34**, 904. A. Fahrner, D. R. P. 183703; abst. Chem. Zentr. 1907, **78**, II, 652. W. Feld, E. P. 21996, 1911; abst. C. A. 1913, **7**, 1084. D. R. P. 262326, 1911; abst. C. A. 1913, **7**, 3646. G. Fortier, U. S. P. 1044369. C. Getchell, U. S. P. 378673, 1888. H. Glover, E. P. 3774, 1879. P. Grimm, U. S. P. 924980, 957418; abst. C. A. 1910, **4**, 2357. M. Hanahan, U. S. P. 1253238; abst. C. A. 1918, **12**, 747. J. Herreshoff, U. S. P. 969868; abst. C. A. 1910, **4**, 3285. A. Hinzke, U. S. P. 1149765, 1915; abst. J. S. C. I. 1915, **34**, 960. H. Humphries, E. P. 11750, 1912; abst. J. S. C. I. 1912, **31**, 1124. D. Hunt, E. P. 18895, 1911; U. S. P. 1053915, 1913; abst. J. S. C. I. 1912, **31**, 921; 1913, **32**, 289. J. Jones, U. S. P. 872822, 1907; abst. J. S. C. I. 1908, **27**, 23. P. Lehmann, D. R. P. 291426; abst. J. S. C. I. 1916, **35**, 691. I. Loeser, E. P. 4385, 1875. C. Lyman, U. S. P. 911753; abst. C. A. 1909, **3**, 1065. J. Marsden, A. Paul and A. Tromblee, U. S. P. 749311. G. Miller, U. S. P. 1018255, 1912; abst. J. S. C. I. 1912, **31**, 333. W. Maynard, E. P. 6982, 1884. H. Niedenführ, D. R. P. 249330; abst. J. S. C. I. 1912, **31**, 773. E. Nemethy, D. R. P. 48285. Pintsch Akt. Ges. D. R. P. 295747, 1915; abst. J. S. C. I. 1917, **36**, 646. G. Oddo, E. P. 21255, 1908; D. R. P. 225321; F. P. 397450; Chem. Ztg. 1910, **34**, 505, 514. Pratt Engineering & Machine Co., E. P. 118097, 1918; abst. C. A. 1919, **13**, 1. E. Rossiter, U. S. P. 1038442, 1039812; abst. J. S. C. I. 1912, **31**, 983, 1031; C. A. 1912, **6**, 3499. C. Savage, U. S. P. 841576. Chem. Fabr. auf Actien vorm. Schering, D. R. P. 191596, 1907; abst. J. S. C. I. 1908, **27**, 502. A. Schimmel, Arch. Suikerind. 1916, **24**, 1820; abst. C. A. 1918, **12**, 743. A. Seyferth, E. P. 756, 1869. D. Whalen, U. S. P. 1065750. G. Stebbins, U. S. P. 934700. Thalín, Nor. P. 20450. O. Witt, D. R. P. 186332; abst. C. A. 1908, **2**, 166. J. Tufts, U. S. P. 891115. C. Weatherby, E. P. 4161, 1873. Wynne, Australian P. Appl. 1844, 1905. Anon., Chem. Eng. **9**, 71; abst. C. A. 1909, **3**, 1575. G. Huft, Can. P. 190870, 1920.

agitation of the sulfur by paddles, blowing jets of air and steam over the sulfur, and devices for regulating the heat.

The temperature in a sulfur burner operating with air and furnishing a gas containing 10% SO_2 has been calculated¹ to be 900°. Actual measurements with a Le Chatelier pyrometer gave the following results with a simple pan burner:

(1) Temperature in space above pan 10 mins. after charging, 340°, after 85 mins., 495°.

(2) Temperature in space above pan after 15 mins., 370°, after 25 mins., 420°.

(3) Temperature in space above pan after 90 mins., 520°. It is assumed that the best temperature is 330°-340°.

A type of mechanical burner in considerable use is that of Tromblee and Paull, made by the Glen Falls Machine Works, N. Y. The following particulars relate to these burners, in the standard sizes:

| | S Burned per Hour Lbs. | Approx. Weight Lbs. | Floor Space |
|---|------------------------------|---------------------------|----------------|
| No. 1. Short Special, 20 in. diam. shell, 4 ft. long..... | 35 | 3500 | 8 x 6 ft. |
| No. 2. Special, 20 in. diam. shell, 8 ft. long..... | 65 | 4200 | 12 x 6 ft. |
| No. 3. Small, 30 in. diam. shell, 8 ft. long..... | 130 | 4900 | 12 x 6 ft. |
| No. 4. Standard, 36 in. diam. shell, 8 ft. long..... | 250 | 8200 | 16 x 7 ft. |
| No. 5. Short large, 48 in. diam. shell, 8 ft. long..... | 400 | 12300 | 20 x 10 ft. |
| No. 6. Large, 48 in. diam. shell, 16 ft. long..... | 800 | 15500 | 28 x 10 ft. |

1. S. Pagliani, *Ann. chim. applicata*, 1915, **4**, 75; abst. J. S. C. I. 1915, **34**, 1050; C. A. 1915, **9**, 331. In this connection Experimental Report No. 43, H. M. Factory Gretna, on the operation of S burners, will be of interest. See also Exptl. Report No. 22. The following patents on sulfur burners may be consulted: U. S. P. Reissue 12921 to 835926. U. S. P. 20755, 52090, 86881, 95307, 101011, 123713, 127008, 134389, 137692, 143202, 180901, 183185, 185964, 187413, 188801, 191778, 197474, 234025, 268530, 268793, 284817, 308289, 309968, 311595, 319168, 337197, 338557, 361761, 363457, 376883, 392235, 410415, 412664, 414051, 421076, 421201, 451651, 471618, 475824, 485126, 490981, 542429, 572193, 623807, 661496, 661497, 678179, 685779, 704412, 711485, 715778, 734397, 749311, 783783, 788512, 802191, 810063, 829765, 835926, 841576, 866635, 872822, 885891, 891115, 900500, 906574, 911735, 924980, 934700, 952098, 952099, 952100, 952970, 957418, 981625, 996215, 1018255, 1024798, 1027022, 1038442, 1039464, 1039812, 1044369, 1065750, 1078937, 1110454, 1215636.



FIG. 87.—SULFUR STORAGE (H. M. FACTORY GRETNA)



FIG. 88.—WEIGHED SULFUR CHARGES TO BE BURNED

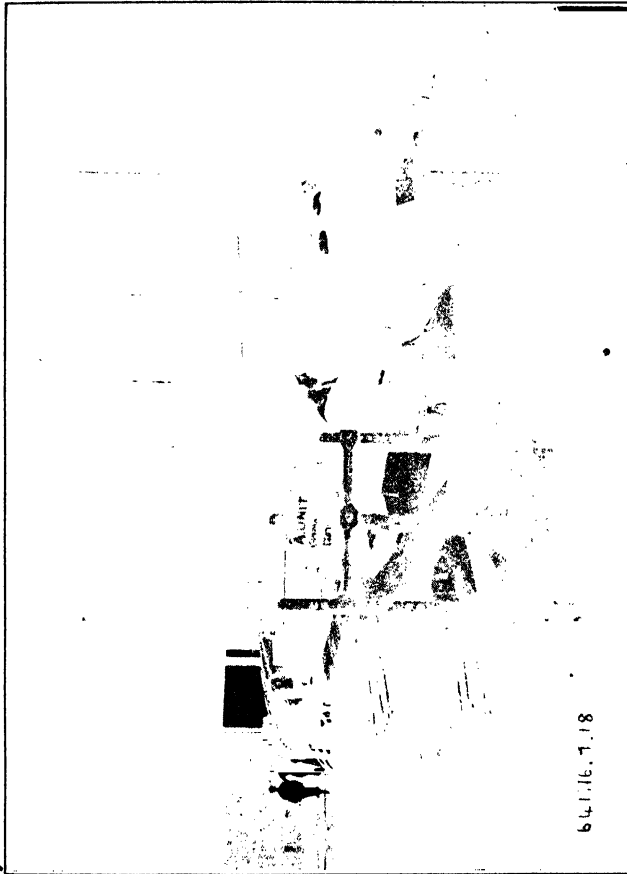


FIG. 89.—SULFUR BURNERS IN OPERATION (H. M. FACTORY, GREINA)

The shell of the burner is of flanged steel, the cast-iron heads are cone-shaped and their flanges form the bearings. The rolls or trunnions, foundation plates and pulley standard are of cast-iron. The combustion chamber of the Standard burner is either a cast-iron box, 30 in. wide, 44 in. high, and 48 in. long, or a closed circular steel tank, 6 ft. in diameter, 10 ft. high, lined with special firebrick. The neck at the back of the burner passes into the chamber. An opening on the opposite side of the cast-iron chamber, covered with a plate, is for the purpose of reversing the chamber when convenient. The pipe connection to the cooler is made from the top of the combustion chamber, and dampers are provided in the chamber and in the feeding doors for the regulation of the supply of air. A door at the back is provided for cleaning out the ash.

Sulfur is fed automatically to the burner through the front end of the machine, the burner shell rotating at the rate of half a revolution per minute. Half a horse-power is required. As the burner rotates, the sulfur is carried over, forming a complete coating on the inside of the shell. The whole of this coating is undergoing combustion, and a high temperature and perfect combustion are said to result.

The gas produced may contain as high as 18% SO_2 . Where Louisiana sulfur is used there is practically no residue left in the burner. The action is easily regulated and then becomes automatic.

Another type of mechanical burner is the Vesuvius burner, made by the Valley Iron Works Co., Appleton, Wis. This is a modification of the old shelf burner, but the feed is automatic. It is vertical, constructed of iron with a lining of firebrick. At the top is a melting kettle. Inside are a number of iron trays or shelves, resting loosely on the brick lining. The gas outlet consists of two parts, an oblong 45° elbow, extending about 4½ in. into the burner, and a round iron pipe, oblong shaped at one end to conform with the elbow, and slotted in the upper part to serve as a combustion chamber. Around this slotted pipe is a circular damper.

The advantages claimed over the rotary burner are the smaller floor-space required, the absence of mechanical drive for turning, and the more certain feed with liquid sulfur. The burner

consumes a maximum of nine tons of sulfur per 24 hours, requiring a floor-space of 72 sq. ft. Each of the five stages is provided with a door for regulation of the air supply. The burner is now made in nine different sizes, the largest with 9 tons capacity per 24 hours, and the smallest 1 ton per 24 hours.

Sulfur Dioxide, SO_2 , is a gas at the ordinary temperature, of density 1.434 gm. per liter at 0° and 760 mm. It is easily condensed to a liquid by cooling, or by three atmospheres compression at the ordinary temperature. The b. pt. of the liquid is -10.1° ; m. pt. of the solid, -76° . The liquid dissolves sulfur, iodine, phosphorus, resins, and many other substances insoluble in water. Liquid sulfur dioxide is made on a large scale, and transported in glass syphons or iron cylinders.

Sulfur dioxide may be made on a small scale by heating strong sulfuric acid with copper or carbon: $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$; $\text{C} + 2\text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + \text{CO}_2 + 2\text{SO}_2$. In the latter case, acid of 165° Tw. and iron vessels are used. The carbon dioxide is not detrimental, since the SO_2 is usually absorbed in water, in which CO_2 is sparingly soluble.¹

For the production of the gas by burning sulfur in air the types of burner previously described (p. 1062) may be used. Smaller scale burners are also employed, of which there are several kinds.² The

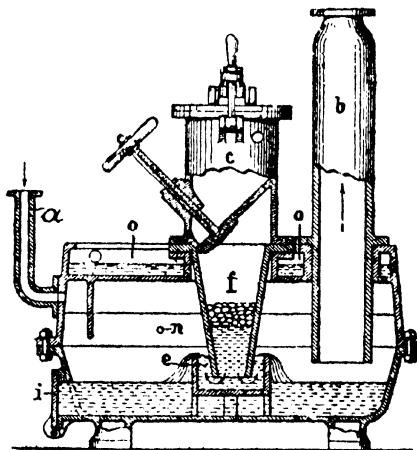


FIG. 90.—THE SACHSENBURGER SO_2 BURNER (Fig. 90) is made of cast-iron. The sulfur is introduced at *i*, and the door closed. It is kindled by a red-hot iron rod inserted through *n*,

1. See J. Grayson, E. P. 132387, 1918; abst. J. S. C. I. 1919, **38**, 817-A.
2. L. Descamps, U. S. P. 1254992, 1918; abst. J. S. C. I. 1918, **37**, 182-A; C. A. 1918, **12**, 749; E. P. 100939, 1916; abst. J. S. C. I. 1916, **35**, 963. P. Grimm, E. P. 10774, 1909; U. S. P. 957418; abst. J. S. C. I. 1910, **29**, 352. J. Westgate, E. P. 17348, 1909; abst. J. S. C. I. 1910, **29**, 695. P. Contamin, U. S. P. 996215, 1911; abst. C. A. 1911, **5**, 2706. C. Clark, U. S.

the air being supplied through the pipe *a*. Sulfur dioxide escapes through *b*, while molten sulfur collects on the bottom of the furnace. Fresh sulfur is introduced through *c* into the funnel *f*, the lower end of which projects into the burner. There is a plate rotated by a handle in *f* which regulates the supply of sulfur. The upper part of *f* is water-cooled, as shown at *o*. Compressed air may be introduced into *b* to burn any residual sulfur.

The Körting burner consists of a pan in the lower part, in which sulfur is melted. Air is drawn over the sulfur by a steam injector, and the gas is cooled. This is made in three sizes for 10, 20 or 40 lbs. S per hour, and is specially intended for the manufacture of sulfites and bisulfites, the gas being absorbed in an alkaline solution in washers.¹ Large quantities of wood-pulp are worked up by means of these sulfite solutions.²

Pyrites Burners are of three main types, according as they are used for (1) lumps, (2) powder, or (3) mechanical burners.

The common lump burners,³ designed for hand-charging, are simple brickwork fireplaces with bars on which the ore rests. Kindling is effected by a little red-hot coke placed on the top of the ore. The thickness of the pyrites bed is about 20 in., and the air supply is carefully regulated by sliding doors below. The regulation of the air supply is most important, since with too

P. 952098, 952099, 952100, 1910; abst. Chem. Ztg. Rep. 1910, **34**, 342. F. Clayton, D. R. P. 194948; abst. Zts. ang. Chem. 1908, **21**, 931; Chem. Zentr. 1908, **79**, I, 1107; Jahr. Chem. 1905-1908, I, 1527; Wag. Jahr. 1908, **54**, I, 368. W. Feld, E. P. 21996, 1911; abst. J. S. C. I. 1912, **31**, 489. Australian P. 17451, 1910. C. Lyman, U. S. P. 911735, 1909; abst. Chem. Ztg. Rep. 1909, **33**, 145. Sachsenburger Akt.-Maschinenfabr. u. Eisengiesserei, D. R. P. 196371, 1907; abst. J. S. C. I. 1908, **27**, 563. Chem. Fabrik auf Actien. vorm. Schering, D. R. P. 191596; abst. Zts. ang. Chem. 1908, **21**, 793; Chem. Zentr. 1908, **79**, I, 314; Jahr. Chem. 1905-1908, I, 1557; Chem. Zts. 1908, **7**, 536; Chem. Ztg. Rep. 1908, **32**, 24; Wag. Jahr. 1907, **53**, I, 328; Mon. Sci. 1910, **73**, 67, 142.

1. J. Edmunds, U. S. P. 711485; abst. J. S. C. I. 1902, **21**, 1534. M. Kaltenbach, E. P. 107589, 1917; abst. J. S. C. I. 1918, **37**, 301-A. National Chemical Machine and Mfg. Co., E. P. 4337, 1883. W. Wenzel, U. S. P. 704412, 1902; abst. J. S. C. I. 1902, **21**, 1027.

2. See Papierztg. 1894, 1478, 1830.

3. M. Hasenclever, Chem. Ind. 1895, **18**, 494. Stassfurter Chemische Fabrik, vorm. Vorster & Grüneberg, D. R. P. 100708. A. Zavelberg, D. R. P. 170602. F. Falding, Mind. Ind. **7**, 666. A. Znaaer, Zts. ang. Chem. 1907, **20**, 6. J. Addie, E. P. 180, 1886. J. Hargreaves, T. Robinson & G. Hargreaves, E. P. 5681, 1886. United Alkali Co., E. P. 7915, 1905. Haeg, Berg. u. Hüttenm. Ztg. 1893, 383. O. Battaille and P. Piperaut, E. P. 2367, 1912; U. S. P. 1089304. N. Akin, U. S. P. 127008, 1872. J. Albrecht, U. S. P. 20755, 1858. See Exptl. Rep. No. 25, H. M. Factory, Gretna, on the operation of pyrites burners.

much air the furnace becomes cooled, and with too little air sublimation of unburnt sulfur occurs, together with clinkering of the pyrites. About 70–90 cu. ft. of air per lb. of pyrites is used, depending on the sulfur content, the draught being regulated so that the sulfur flames rise vertically from the red-hot bed and tend to blow outwards when the inspection door is opened. The temperature of the gases leaving the burners is 400°–500°. By turning the loose firebars with a key, the burnt pyrites is let down into a cavity below, called the burnt ore den, where it cools. In such burners about 10 cwt. of pyrites is burnt per kiln per 24 hours, or 5 cwt. per sq. yard of grate surface per 24 hours.

The lump pyrites is first broken into pieces of suitable size in jaw-crushers. In England the pieces pass a 3 in. sieve, but as little smalls as possible are made. The smalls and pieces are often burnt separately, although in modern breakers only so much smalls is produced as can be burnt with the lumps in the above burners. Special types of crushers have been devised.¹

Pyrites powder, or "smalls," is burnt in shelf furnaces, such as those of Maletra or Delplace,² consisting of a series of hearths over which the powder is raked, dropping from hearth to hearth in succession. Ignition is started by heating on a separate hearth, which is then bricked up, the burnt ore dropping into a den below. In Maletra furnaces about 13 cwt. of pyrites are burnt per 24 hours, or about 2 cwt. per sq. yard of grate surface per 24 hours. The major portion of the burning takes place on the second shelf from the top.

In modern works, mechanical burners are mostly used. Some of these consist of large flat hearths³ over which cars or rabbles are

1. Märkische Maschinen Fabrik, D. R. P. Oct. 16, 1877; see Dingl. Poly. 1877, **227**, 58. The Humboldt Engineering Co., D. R. P. 1906, 1878. Brown, Sci. Amer. 1879, 194. Welter, D. R. P. 7494, 1879. P. Müller, D. R. P. 295170. G. Polysius, D. R. P. 295035.

2. J. Mactear, E. P. 3701, 1878. E. Bramwell, D. R. P. 22758. G. Lunge, Zts. ang. Chem. 1896, **9**, 63, 157. M. Finch and W. and S. Willoughby, E. P. 2913, 1883. W. Crowder, J. S. C. I. 1891, **10**, 298. See also G. Benjamin, D. R. P. 274663. W. Buddaeus, U. S. P. 1079897. H. Petersen E. P. 15941. 1907; abst. J. S. C. I. 1908, **27**, 904.

3. C. Bartsch, Wag. Jahr. 1886, **32**, 256. G. Lunge, Zts. ang. Chem. 1894, **7**, 134. F. Lütty, Zts. ang. Chem. 1905, **18**, 1253. B. Kauffmann, Zts. ang. Chem. 1905, **18**, 1628. O. Mühlhäuser, Zts. ang. Chem. 1910, **23**, 347. E. Hegeler, U. S. P. 303531, 592006. Chem. Fabrik Rhenania, D. R. P. 610433. Encke, D. R. P. 211433. P. Spence, E. P. Dec. 24, 1878. D. R. P. 9267. U. S. P. 248521. E. P. 1494, 1882. P. Spence and T. Illingsworth, E. P. 2840, 1878. Fusina, D. R. P. 288477.

drawn by chains, and although they require but little manual labor, they readily get out of order. The most used type of mechanical burner is one of the numerous modifications of the MacDougall furnace, in which the ore is fed into a cylinder provided with shelves over which scrapers fitted to a shaft (usually air or water cooled) revolve, pushing the ore from shelf to shelf until all the sulfur is consumed. Well-known types are the Herreshoff¹ and the Wedge burner. This latter has a hollow

1. S. Barth, D. R. P. 289259, 291886. Chem. Apparatur, 1915, **2**, 95, 105. Chem. Ztg. 1914, **38**, 816. E. Bracq-Laurent and R. Moritz, F. P. 390838, 1908; abst. J. S. C. I. 1908, **27**, 1111. A. Düron, D. R. P. 275751; D. R. P. Anm. D-28657. G. Lunge, Zts. ang. Chem. 1894, **7**, 15. J. Harris, D. R. P. 247695, 259208, 273045. F. P. 432121; E. P. 23331, 28078, 1911; 21897, 1913. W. Hall, E. P. 20759, 1912; New Zeal. P. 33718, 1913. U. S. P. 1076763, 1913; abst. J. S. C. I. 1913, **32**, 1009, 1109. H. Koppers, D. R. P. 288322. A. McDougall, E. P. 270, 1868. Metallbank und Metallurgische Ges., D. R. P. 263939, 268602, 273942, 288105; D. R. Anm. M-50050, 53925. Nichols Copper Co. and H. Stout, E. P. 9958, 1915; abst. J. S. C. I. 1915, **34**, 1150. J. Parent, F. P. 424269, 1910; abst. J. S. C. I. 1911, **30**, 894. Spinzig & Hommel, D. R. P. 272097, 290835. F. P. 460128. Aust. P. 67690. D. R. P. 292487. P. Truchot, Rev. chim. 1914, **17**, 169. Erzröst-gesellschaft Köln, D. R. P. 246067, 250310, 262002, 267374, 268649. A. Tangye, E. P. 817, 1900. U. Wedge, U. S. P. 1123965, 1123966, 1915; abst. J. S. C. I. 1915, **34**, 234. D. R. P. 255648.

See also L. Anderson, Eng. Min. J. 1914, 51, 258; U. S. P. 1123965, 1123966. R. Zelewski, D. R. P. 142435. F. Trego, U. S. P. 798844. W. Hommel, D. R. P. 204423. E. Hartmann and F. Benker, Zts. ang. Chem. 1906, **19**, 1125, 1188. See Chem. Ind. 1911, **34**, 561. M. Kauffmann, D. R. P. 161624, 163914, 165270, 186314, 186315, 205215, 227621. Erzröstges., Aust. P. 51096. K. Reusch, Chem. Ztg. 1912, **36**, 213. U. Wedge, U. S. P. 648183, 654335, 777577, 842736, 976525. R. Mackenzie, E. P. 4418, 1881. Hering, D. R. P. 9634. T. Mason, E. P. 3196, 1880. T. Walker and J. Carter, E. P. 4000, 1883; see Eng. Min. J. **37**, 294. Cf. W. Martyn, J. S. C. I. 1885, **4**, 26. W. Brückner, Eng. Min. J. **37**, 425; abst. Wag. Jahr. 1884, **30**, 221. R. and C. Oxland, E. P. 1447, 1870; E. P. 7285, 1885. J. Herreshoff, U. S. P. 556750, 1896; 616926, 1899; 729170, 1903; 976175, 1910. Cf. Mineral Ind. **6**, 236; P. Gilchrist, J. S. C. I. 1899, **18**, 459. U. S. P. 976175. F. P. 420975. D. R. P. 243325. F. Quince, Zts. ang. Chem. 1910, **23**, 1922. F. Winteler, Chem. Ztg. 1906, **30**, 467. W. Simons, D. R. P. 166569. H. Howard, E. P. 21762, 1905. A. Legge, E. P. 21160, 1905. Maschinenbau-Anstalt Humboldt, E. P. 27061, 1906. F. Timm, D. R. P. 195670. J. Greenawalt, D. R. P. 182409. F. Klepetko, D. R. P. 185003. Hegeler, Min. Ind. 1905, 246. E. Hartmann and F. Benker (Ducco's furnace), Zts. ang. Chem. 1906, **19**, 1194; D. R. P. 185809. Eisenwerk Laufach, D. R. P. 185673. W. Warren, E. P. 17457, 1905; U. S. P. 864816. C. Pfaul, D. R. P. 177963. F. Falding, E. P. 6931, 1905. A. Woeke, D. R. P. 210657. F. Schlippenbach, D. R. P. 225421; E. P. 28755, 1909; F. P. 415920. H. Daniel and H. Römer, D. R. P. 208354. E. Collet and M. Eckardt, Norw. P. 20273. R. Zelewski, D. R. P. 195724; D. R. Anm. Z-5379. J. Tafto, U. S. P. 891116; D. R. P. 207760. S. Beuve and E. Marconnet, F. P. 390323. O. Nidenführ, D. R. P. 239702, 239703. Special contrivances for charging the ore into the furnaces, Metallbank und Metallurgische Ges., D. R. Anm. M-42726. Maschinenbauanstalt Humboldt, D. R. Anm. M-43170. Svolvysre and Superphosphat Fabrik, E. P. 28703, 1911. Scherfen-

revolving shaft, 4 ft. diameter, to which the rakes are attached, the shaft and arms being cooled by a draft of air from fans. The teeth of the rakes are easily renewable. A furnace of 20 ft. diameter roasts 12 tons of pyrites in 27 hours, requiring $1\frac{1}{2}$ h. p. The ore is fed into the top and descends, first outwards and then inwards, on alternate floors, being met by ascending air. The larger sizes burn 20 tons of pyrites in 27 hours. The chief drawback to mechanical burners is the large amount of dust they produce, necessitating efficient dust catchers. Dust is also formed by all burners, but to a less extent in lump ore burners than in

berg & Prager, D. R. P. 329759, 332056. W. Hommel, F. P. 384350. Aktienges. f. Bergbau, Blei u. Zinkfabrikation, D. R. P. 202377. T. Merton, D. R. P. 185506. E. Bracq-Laurent, D. R. P. Ann. B 52816. Grünwald & Welsch, D. R. P. 232044. Bragg & Moritz, D. R. P. Ann. B 52486. J. Parent, F. P. 421269. X. de Spirlet, D. R. P. 236089. R. Scherfenberg, D. R. P. 236090, 237215. R. Hübner, D. R. P. 236669. J. Harris, E. P. 23331, 1910. C. Renwick, U. S. P. 981880; D. R. P. 216180. Metallbank u. Metallurgische Ges., D. R. P. 243913; E. P. 19314, 1911. Maschinenbauanstalt Humboldt, D. R. P. 213613. Soc. minière et métallurgique de Penarroya, D. R. P. 275908. Bracq, D. R. P. 250623, 257424; E. P. 20108, 1912. Wagenmann, Seybel & Co., Aust. P. 54964. J. Jones, D. R. P. 263393, U. S. P. 1097177; abst. Oest. Chem. Ztg. 1917, **20**, 13. Kirsch & Mauser, D. R. P. 263851. E. Gottlieb, D. R. P. 268330. C. Thorsell, Norw. P. 34440. A. Gaillard, F. P. 458113. Helsingborgs Kopparverks, D. R. P. 261608. Kalinowsky and Roth, D. R. P. Ann. K-29006. E. Dohet, D. R. P. 258261, 265075. Aust. P. 67180. R. Scherfenberg, D. R. P. 258766. H. Stout, E. P. 3581, 15463, 1914. J. Parent, D. R. P. 264709. Wocke, D. R. P. 216657. E. Fowler, E. P. 7471, 1914. J. Claude, F. P. 468968. A. Herzog, U. S. P. 1108906. Timm, Aust. P. Ann. 9226, 1913. A. Ramen and K. Beskow, E. P. 12214, 1911; D. R. P. 253320. T. Edwards, D. R. P. 242888, 250774, 255747. Ernest, Aust. P. Ann. 2496. Chem. Ind. Akt. Ges. and L. Singer, D. R. P. 262610. S. and G. Dumont, D. R. P. 262183. E. Bousse, D. R. P. 280523. W. Hall, E. P. 20759, 1912; U. S. P. 1076763. H. Ridge, E. P. 23763, 1912. A. Zetsche, D. R. P. 280430. A. Zavelberg, U. S. P. 1107006; F. P. 468685; D. R. P. 284607, 292809. P. Sarrasin, E. P. 26915, 1913; F. P. 451182. A-G f. Zinkindustrie vorm., W. Grillo and W. Scheffzik, D. R. P. 280427, 280429. Sela A-G., D. R. P. 285913. J. Lütgens and W. Ludewig, D. R. P. 262128; F. P. 449144; U. S. P. 117670. Nichols Copper Co., D. R. P. 276570, 284586, 286381, 287079, 288013, 289990 and D. R. P. Ann. 15180. Nichols Copper Co. and Stout, E. P. 9958, 1915. K. Hildebrandt, D. R. P. 290733. Maschinenfabrik A. G. vorm. Wagner & Co., D. R. P. 290534, 291239. H. Jenks, U. S. P. 1179928. W. Mount, U. S. P. 1179952. X. de Spirlet, D. R. P. 292371. W. Hommel, D. R. P. 292794.

For further information consult: Zellweger, Eng. Min. J. 1900, 301. R. Zelewski, D. R. P. 195724, 201191. A. Merton and H. Ridge, E. P. 13625, 1909; 3843, 3981, 1911. M. Hasenclever, J. S. C. I. 1911, **30**, 1291. E. Schütz, Metallurgie, 1911, 637. A. Nemes, Metallurgie, 1912, **7**, 516. Anon., Papierztg. 1903, **28**, 288; abst. J. S. C. I. 1903, **22**, 251. J. I. E. C. 1918, **10**, 293.

1. J. Berreshoff, D. R. P. 143740. Metallbank und Metallurgische Ges. A. G., F. P. 456524. E. Heine, D. R. P. 280088. R. Reichling, D. R. P. 279819. C. Mobre, U. S. P. 1184006. Brunner & Co., D. R. P. 269539.

mechanical burners which are equipped for the roasting of powder.

The dust-catchers vary considerably with the different kinds of plants. One form consists of brickwork chambers with transverse baffle-walls, and another of a brickwork tower filled with broken bricks supported on bars which can be dropped from time to time and fresh bricks put in. A point to be kept in mind in the design of dust-catchers is to avoid any unnecessary cooling of the gas from the pyrites burners, since the heat is required in the Glover tower following this part of the plant.

Proposals to utilize "smalls" by agglomerating them into briquettes¹ cannot be said to have found any extensive application. Roasting in inclined tube-furnaces has also been proposed.²

The reaction in the roasting of pyrites is the conversion of the iron into ferric oxide and of the sulfur into sulfur dioxide: $4\text{FeS} + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$. In contact with iron oxide, a portion of the SO_2 is further oxidized to SO_3 . The burner gas contains 6%-11% by volume excess oxygen, and 7%-8% SO_2 , as against 10%-11% from brimstone burners. From 3%-5% of the total sulfur is usually in the form of SO_3 or H_2SO_4 mist. The scientific principles of roasting have been discussed by R. Schenck.³

The pyrites-cinder from the kilns usually contains 0.75%-3% of sulfur, which is essential if the copper is to be extracted by the wet process. In the case of non-cuprous ores, the roasting should aim at eliminating as much sulfur as possible. The burnt ore, after extraction of the copper or directly, is then heated in revolving kilns called nodulizing kilns, to remove the residual sulfur, and then smelted in the blast-furnace. Attempts to smelt

Gerdt & Strauch, D. R. P. 257368. C. Watson, E. P. 17384, 1912. M. Neumark, D. R. P. 263285. W. Greding, D. R. P. 263201. H. Pünning, D. R. P. 262882. A. Müller, D. R. P. 216483, 265638. M. Kirschner, D. R. P. 268880. Krowatschek, D. R. P. Anm. K-45381. U. Wedge, E. P. 16617, 1915. V. Alcher, D. R. P. 289569. Egestorff's Salzwerke, D. R. P. 70396. C. Vadner, U. S. P. 1110660. W. Hommel and H. Durant, E. P. 28611, 1909. H. Rehmann and A. Mirbach, D. R. P. 292004.

1. H. Wurtz, U. S. P. 252287; abst. J. S. C. I. 1882, **1**, 67. J. Wiess, D. R. P. 185602. J. Robeson, E. P. 1639, 1908; D. R. P. 238119; F. P. 386695. U. Wedge, U. S. P. 804690, 804691, 804785; D. R. P. 181516. P. Ricketts and T. King, U. S. P. 894799. G. Polysius, D. R. P. 262241. C. Brackelsberg, Zts. ang. Chem. 1916, **29**, I, 281. R. Zelewski, U. S. P. 1097500. A. Anderson, F. P. 458442; Belg. P. 256447.

2. R. and C. Oxland, E. P. 7285, 1885. J. Jones, U. S. P. 1097177, 1914; abst. J. S. C. I. 1914, **33**, 961. S. Peacock, U. S. P. 1009559, 1911.

3. Zts. ang. Chem. 1913, **26**, 510, 646; abst. C. A. 1914, **8**, 483; J. C. S. 1913, **104**, ii, 1057; Chem. Zentr. 1913, **84**, II, 2176. Wag. Jahr. 1913, **59**, I, 211.

pyrites directly for iron, with utilization of the sulfur dioxide, have also been made.^{1,2}

Sulfur Dioxide from Copper Pyrites. Sulfur dioxide evolved

1. J. Channing and F. Falding, U. S. P. 962493; abst. C. A. 1910, **4**, 2552. E. P. 12138, 1910; D. R. P. 250772, 253492, F. P. 416988; abst. C. A. 1913, **7**, 541; J. S. C. I. 1910, **29**, 1380. Eng. Min. J. 1910, **90**, 555; abst. C. A. 1909, **3**, 2981; J. S. C. I. 1910, **29**, 1387. Cf. H. Koppers, D. R. P. 288322, 1913; abst. J. S. C. I. 1916, **35**, 360; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111, 112. R. Hill, U. S. P. 847664, 1907; abst. J. S. C. I. 1907, **26**, 474. H. Stout, U. S. P. 1181183, 1181184, 1916; E. P. 9958, 1915; abst. J. S. C. I. 1915, **34**, 1150; 1916, **35**, 695.
2. For further information on this subject, consult: H. Achenbach, D. R. P. 252412, 286601. J. Addie, E. P. 180, 1886. C. Allhusen, E. P. 789, 1867. U. Alvisi, E. P. 23493, 1900. H. Angel, E. P. 24136, 1904; abst. J. S. C. I. 1905, **24**, 200. F. van Berckelaer, F. P. 384904, 1907; abst. J. S. C. I. 1908, **27**, 503. W. Blinkhorn, E. P. 1084, 1878. A. and L. Brin, E. P. 12070, 1886; abst. J. S. C. I. 1887, **6**, 597. W. Buddeus, D. R. P. 285888. A. Carmichael and H. Montgomery, E. P. 14295, 1914. J. Channing, E. P. 12137, 12138, 1910. T. Cobley, E. P. 4755, 1878. Cic. Par de Coul. d'Aniline, F. P. 318932, 1902; abst. J. S. C. I. 1902, **21**, 1454. C. Debuch, D. R. P. 269774. G. Duryee, E. P. 5457, 1880. B. Eldred, U. S. P. 885328, 1908; abst. J. S. C. I. 1908, **27**, 509. A. and W. Elmore and H. Barrett, E. P. 15988, 1885. J. Fleming, E. P. 10153, 1887. G. Fusina, E. P. 8426, 1912; F. P. 442280, 1912; abst. J. S. C. I. 1912, **31**, 931; 1913, **32**, 541. A. Germet and H. Fievet, E. P. 2407, 1901; abst. J. S. C. I. 1902, **21**, 176. J. Greenawalt, U. S. P. 904060, 1908; abst. J. S. C. I. 1908, **27**, 1210. G. Gröndal, D. R. P. 277895. W. Hall, U. S. P. 1133637, 1134846; abst. J. S. C. I. 1915, **34**, 557. F. P. 455474, 455475, 455905, 1912; abst. J. S. C. I. 1913, **32**, 943. J. Hanson, E. P. 1393, 1888. J. Hargreaves and T. Robinson, E. P. 1923, 1928, 1871; 5681, 1886. M. Hanahan, U. S. P. 1253238, 1918; abst. J. S. C. I. 1918, **37**, 148-A. H. Humphries, E. P. 17232, 1915; abst. J. S. C. I. 1917, **36**, 83. R. Hübner, U. S. P. 906883, 1908; abst. J. S. C. I. 1909, **28**, 95. S. Holroyd, E. P. 565, 1869. H. Howard and F. Stantial, U. S. P. 1271899; abst. C. A. 1918, **12**, 1913. G. Haglund and A. Grönningaeter, U. S. P. 1163234, 1915; abst. J. S. C. I. 1916, **35**, 125. H. Hilbert, E. P. 9493, 1903; abst. J. S. C. I. 1903, **22**, 1085. W. Hughes, E. P. 4496, 1880. J. Hollway, E. P. 4549, 1878, 1131, 1878. F. Johnson, U. S. P. 873943, 1907; abst. J. S. C. I. 1908, **27**, 128. G. Kingsley, U. S. P. 1144480, 1915; abst. J. S. C. I. 1915, **34**, 834. G. Keppeler, Chem. Ztg. 1913, **36**, 1219. See P. Uhlmann, Chem. Ztg. 1914, **37**, 59. E. Knudsen, E. P. 20560, 1901; abst. J. S. C. I. 1902, **21**, 123. F. Knowles, E. P. 603, 1884. C. Leech and T. Neal, E. P. 1281, 1878. P. Lehmann, D. R. P. 291426, 1914; abst. J. S. C. I. 1916, **35**, 691. W. Martin, D. R. P. 272918. G. Marks, E. P. 6724, 1903; abst. J. S. C. I. 1903, **22**, 1352. I. McDougall, E. P. 1349, 1883. R. Mallett and H. Scholefield, E. P. 2952, 1872. J. Mason, E. P. 4310, 1878. U. S. P. 274453, 1883. Nichols Copper Co., D. R. P. 288013. R. Pictet, E. P. 480294, 1915; abst. J. S. C. I. 1917, **36**, 133. G. Rambaldini, E. P. 2402, 1902; abst. J. S. C. I. 1903, **22**, 145. J. Robeson, E. P. 1639, 1908. G. Rigg, U. S. P. 1103081, 1914; abst. J. S. C. I. 1914, **33**, 870. C. Renwick, E. P. 426149, U. S. P. 981880, 1911; abst. J. S. C. I. 1911, **30**, 220. 962. P. Spence, E. P. 2823, 1870. J. Spence, E. P. 1855, 1879. A. Sebillot, E. P. 1913, 1882. P. Spinzig and A. Wannag, D. R. P. 255454, 1911; abst. J. S. C. I. 1913, **32**, 241. R. Sticht, Proc. Austral. Inst. Min. Eng. 1915, **19**, 75; abst. J. S. C. I. 1916, **35**, 118. W. Tooth and J. Rooker, E. P. 7988, 1884. J. Thwaites, E. P. 27426, 1907; abst. J. S. C. I. 1908, **27**, 949; F. P. 393589; abst. J. S. C. I. 1909, **28**, 91. H. Wurtz, E. P. 4218, 1881. L.

in the smelting of copper pyrites for the production of metal has been successfully utilized in the manufacture of sulfuric acid. The ore is smelted in the blast-furnace for the production of matte, and the gases used in chamber plants. The gases from the converters used in working up the mattes to metal may ultimately be utilized when the proper conditions have been realized.¹ The largest plants using the process are those of the Tennessee Copper Co., the Ducktown Sulfur, Copper and Iron Co., the Anaconda Copper Co., and the Mountain Copper Co., Moroco, Cal.,² all in the United States.

Sulfur Dioxide from Blende. The manufacture of sulfuric acid from the gas evolved in the roasting of zinc blende for the reduction to zinc forms a very important source, especially in American, Belgian and German practice. The reaction is: $\text{ZnS} + \text{O}_2 = \text{ZnO} + \text{SO}_2$, but is liable to be complicated by the

Wright, F. P. 45423; E. P. 26128, 1911; abst. J. S. C. I. 1913, **32**, 29, 541; 1914, **33**, 1061. Oest. Chem. Ztg. 1917, **20**, 13. J. Westergren, Swed. P. 31999; abst. C. A. 1912, **6**, 2302. U. Wedge, U. S. P. 1039464; abst. C. A. 1912, **6**, 3499. H. Wierum, U. S. P. 1182951, 1916; abst. J. S. C. I. 1916, **35**, 743. E. and P. Dutt, India P. 3640, 1918. Zellstoffabrik Waldhof, Norw. P. 29327, 1919; abst. C. A. 1919, **13**, 1375. E. Sutcliffe, E. P. 16450, 1912. J. Symonds and J. Fell, E. P. 883, 1856. A. Sainte-Beuve and G. Marconnet, Belg. P. 200136, 1907. C. Stickney, U. S. P. 493193, 1893. Boyd and Durant, E. P. Appl. 17642, 1919; abst. J. S. C. I. 1919, **38**, 558-A. E. Bracq, E. P. 118094; abst. J. S. C. I. 1919, **38**, 252-A. J. Conrad, U. S. P. 886948, 1908. F. Dochain, Belg. P. 203342, 1907. H. Ellis, U. S. P. 1289417; abst. J. S. C. I. 1919, **38**, 135-A; C. A. 1919, **13**, 774. C. Fish, U. S. P. 451651, 1891; D. R. P. 62216; abst. Wag. Jahr. 1892, **38**, 288. J. Hughes, U. S. P. 65914, 1867. G. Hurt, U. S. P. 1289783, 1918; abst. J. S. C. I. 1919, **38**, 135-A; C. A. 1919, **13**, 773. E. P. 118097, 1918; abst. J. S. C. I. 1919, **38**, 135-A. S. Krotoff, Bull. assoc. chim. suc. dist. 1918, **35**, 102; abst. C. A. 1919, **13**, 2154. J. Marsden, U. S. P. 685779, 1901. A. McIntyre, U. S. P. 1303348, 1919; abst. J. S. C. I. 1919, **38**, 535-A; C. A. 1919, **13**, 1911. S. Smith, U. S. P. 421201, 1890. G. Stebbins, U. S. P. 906574, 1908. A. Tromblee, U. S. P. 885801, 1908. J. Wise, U. S. P. 835926, 1906. Reissue 12921, 1909.

1. E. Larison, Eng. Min. J. 1916, **102**, 1121; abst. C. A. 1917, **11**, 386. W. Belson, Mining Sci. **65**, 149; abst. C. A. 1912, **6**, 917. D. Korda, U. S. P. 1003051, 1911; abst. J. S. C. I. 1911, **30**, 1219. Bull. U. S. Geol. Survey, 1911. J. Channing, U. S. P. 962498; D. R. P. 253492. C. Offerhaus, Metall und Erz, 1914, **10**, 863; abst. Zts. ang. Chem. 1914, **27**, II, 442. C. Debusch, D. R. P. 269774. A. Carmichael and H. Montgomery, E. P. 14295, 1914. W. Norton, Eng. Min. J. 1914, **93**, 299.

2. For further information, see W. Borchers and H. Pedersen, E. P. 9146, 1912. J. Carrick and S. Pattison, E. P. 22166, 1908. H. Ensell, E. P. 2600, 1868. A. Gray, E. P. 2754, 1883. W. Henderson, E. P. 983, 1879. Metals Research Co., and R. Bacon, E. P. 138, 1915; U. S. P. 1151234, 1915; abst. J. S. C. I. 1915, **34**, 1018, 1059. J. Penzance, E. P. 5025, 1882. A. Scbillot, E. P. 20077, 1901. A. Scbillot and G. Dubois, F. P. 384072, 1907; abst. J. S. C. I. 1908, **27**, 404. J. Wilkes and A. Aunier, E. P. 3087, 1874.

formation of sulfate, which is decomposed with difficulty only at higher temperatures than are used in the roasting furnaces. This secondary reaction must therefore be avoided. The roasting of blende differs from that of pyrites in that external heat must be supplied to drive off the sulfur, and special types of furnaces have therefore to be used.

Pure zinc sulfide contains 33% S, while the mineral¹ is usually contaminated with several per cent. of iron as FeS, and frequently manganese. It may contain pyrites and galena, from which it is separated electrically and by flotation. The ore may be given a preliminary flash roast to convert iron into the magnetic oxide Fe₃O₄. If fluorspar is present, wet-concentration should be carefully carried out, as the presence of fluorine in the gases later on will give much trouble. The zinc concentrates at Broken Hill are obtained by flotation processes, which do not, however, remove fluorspar and carbonates.

In treating blende, the ore is roasted in muffle furnaces, with external firing, the first successful furnace of this kind being that of Hasenclever, invented in 1855, at the Rhenania Works. This has repeatedly been improved, and became a commercial success in 1871.

The temperatures at which sulfides begin to lose sulfur dioxide on roasting in air are stated by O. Perret are as follows:

Iron pyrites, 440°

Chalcopyrites, magnetic pyrites, copper matte, 525°

Zinc blende, begins at 750°, complete at 900°

"Speiss," and nickel-copper matte begins at 800°

The gases from blende roasting contain 9% by volume sulfur dioxide, 8% of oxygen, and 83% of nitrogen, double the theoretical amount of air being used. This gives the hypothetical temperature of combustion as 990°, but in practice from 14%-20% of fuel is required, according to the richness of the ore.

The Hasenclever furnace consists² of three superimposed muffles, with heating flues. The temperature of the top muffle is 600°, that of the center muffle 700°, and that of the lower,

1. W. Minor, Chem. Ztg. 1889, **13**, 1602. E. Hänisch and M. Schröder, Chem. Ind. 1884, **7**, 118. P. Truchot, J. S. C. I. 1911, **30**, 207. G. Delplace, D. R. P. 200747. E. Jensch, Zts. ang. Chem. 1894, **7**, 50.

2. R. Hasenclever, Zts. Ver. deutsch. Ing. 1886, 83; abst. Wag. Jahr. 1886, **32**, 257. Chem. Ind. 1899, **22**, 25. K. Eichhorn and M. Liebig, D. R. P. 21032; abst. Wag. Jahr. 1889, **35**, 322. L. Jahne, Zts. ang. Chem. 1894, **7**, 305.

900°. These muffles are 28 ft. long, 4 ft. broad, the height being 6 in. at the edges and 10 in. at the crown of the arch. The fireplace is 32 in. square and burns 5 lbs. of coal per sq. ft. per hour. Each furnace roasts 4 tons of blende per 24 hours, two men being required, normal working being with 26% sulfur in the ore. This falls to 16% at the end of the first muffle, 10% at the end of the second, and 1% at the third. Much heat is carried away by the hot gases and burnt ore.

The following statistics show the increase of blende smelting in the United States in recent years:

| Year | Tons H ₂ SO ₄ Made from Blende |
|------|--|
| 1911 | 230,643 |
| 1912 | 292,917 |
| 1913 | 296,218 |
| 1914 | 411,911 |
| 1915 | 484,942 |

The presence of fluorine in blende gas often leads to corrosion. It is usual to employ two Glover towers, one empty and the other containing lead sheets instead of siliceous packing, or else to circulate all acid made and use a resisting packing. The amount of fluorine in the concentrated acid may be estimated by placing a weighed glass rod in the acid, and weighing at intervals until the loss, due to the formation of silicon fluoride, is constant: $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$.

Other types of blende furnaces (e. g. the Deplace furnace) have been described.¹ Mechanical blende furnaces² have not yet

1. A. Nemes, F. P. 426851. R. Hübner, D. R. P. 236669. Stolberg Actien-Ges., Borchers & Graumann, F. P. 24096, 1906. L. Bemelmans, D. R. P. 76775. M. Perret, D. R. P. 37842. M. Liebig, D. R. P. 237034. H. Petersen, D. R. P. 196216. M. de Lummén, Chem. Trade J. 1916, **58**, 255; **59**, 261.

2. P. Schmieder, D. R. P. 244131. E. Schütz, Chem. Ztg. 1912, **36**, 15. Metallurgie, 1911, 637. Metall u. Erz, 1915, 109. O. Niefenführ, D. R. P. Anm. N-10070. L. Pierron, Mon. Sci. 1900, **55**, 562. R. Trego, U. S. P. 798844. F. Enke, D. R. P. 211433. J. Haas, D. R. P. 23080. M. Hasenclever, J. S. C. I. 1911, **30**, 1291. W. Hommel, D. R. P. 204423. Metallurgie, 1912, 294. K. Eichhorn, D. R. P. Anm. E-18389. H. Ridge, Met. Chem. Eng. 1917, **17**, 215; abst. C. A. 1917, **11**, 3096. Chem. Fabrik. Rhenania, D. R. P. 61043. Soc. Vieille Montagne, D. R. P. 24155, 36609. H. Daniel and H. Römer, D. R. P. 208354. See Eng. Min. J. 1915, **99**, 326, 420.

For further information on mechanical blende roasting furnaces, consult: E. Dohet, D. R. P. 258261; Helsingborg Kopparwerks Aktiebolag, D. R. P. 261605. J. Harris, E. P. 23331, 1910; 7722, 1912. R. Kessler, D. R. P. 270273. Aktien-Ges. f. Zinkindustrie vorm. W. Grillo and W. Schefczik, D. R. P. 280427, 280429, 287078; F. P. 473310. E. Bousse, D. R. P. 280532. T. Edwards, D. R. P. 242688, 255747. N. Heinz and W. Freeland, U. S.

reached the perfection of the pyrites furnaces, but considerable advances have been made in recent years, a number of types being used. The use of mechanical furnaces is imperative in America, where labor is expensive. Important types of furnaces are the Hammond and Spence,¹ the Hegeler,² the Merton,³ the Spirlet,⁴ and the Ridge.⁵ The Wedge furnace (cf. p. 1072) has been used for blende roasting.

The Hegeler furnace consists of hearths over which the blende is rabbled by mechanical stirrers attached to long rods. This furnace occupies a large floor area, because of the runway for the stirrers at each end, a total length of 360 ft. being required. It treats 40 tons of blende per day, with a coal consumption of 25%-30%. The ploughs are drawn through the furnace by chains and, after passing through in one direction, are moved to the next hearth above and drawn through this in the opposite direction, to allow of cooling. The Spirlet furnace, of which several were in operation in Belgium and Germany, and some in America, contains no inside metal parts in contact with the ore, the fuel consumption being low. The alternate hearths rotate and the ore is stirred by special bricks projecting downwards from the hearths above. These bricks have a tendency to break off and choke the furnace, otherwise the results are stated to be satisfactory.

The Ridge furnace has water-cooled stirring shafts, the ore being fed continuously to the drying hearth at the top of the

P. 986700. Nichols Chemical Co., D. R. P. 143740. Maschinenbauanstalt Humboldt, D. R. P. 180263. Enke, D. R. P. 211433. R. Scherffenberg, D. R. P. 237215. W. Tröller, D. R. P. 197258. E. Braeq-Laurent and R. Moritz, D. R. P. 249847. Saccharinfabrik vorm. Fahlberg, List & Co., D. R. P. 257537. J. Lütgens, D. R. P. 260156. Nichols Copper Co., D. R. P. 276570. F. Klepetko, D. R. P. 185003. J. Lütgens and W. Ludewig, D. R. P. 275464. F. Baker, D. R. P. 232895. See also M. Liebig, "Zink und Cadmium," 1913, p. 234.

1. T. Merton and H. Ridge, E. P. 13625, 1909; 3843, 3981, 1911. D. R. P. 253892, 268583. H. Ridge, J. S. C. I. 1917, **36**, 676; Met. Chem. Eng. 1917, **17**, 215; abst. C. A. 1917, **11**, 3096.

2. See O. Mühlhäuser, Zts. ang. Chem. 1910, **23**, 347. M. de Lummen, Chem. Trade J. 1916, **58**, 255; **59**, 261. Eng. Min. J. 1915, **99**, 420.

3. W. Hommel, Metallurgie, 1912, 294; abst. Chem. Zentr. 1912, **83**, II, 67; C. A. 1913, **7**, 1343.

4. X. de Spirlet, F. P. 415338. D. R. P. 236089, 292371. See Eng. Min. J. **98**, 617.

5. T. Merton and H. Ridge, E. P. 13625, 1909; 3843, 3981, 1911. D. R. P. 253892, 268583. H. Ridge, J. S. C. I. 1917, **36**, 676; Met. Chem. Eng. 1917, **17**, 215; abst. C. A. 1917, **11**, 3096.

furnace, passes over three heating hearths, and finally over the cooling hearth, where it preheats the air required for oxidation. The mechanism of each furnace is driven by separate motors. The gases leave the furnace with $6\frac{1}{2}\%$ – $8\frac{1}{4}\%$ SO_2 when Broken Hill concentrates are roasted, the ore being desulfurized to 0.75% of the total sulfur, with a feed of 12 tons of ore per 24 hours, and a coal consumption of 10%.

The chemistry of blende roasting has been discussed in several papers.¹ From the results of experiments, Hommel draws the following conclusions: (1) The ore must be rapidly brought to the temperature of ignition. (2) The ignited blende must be deprived of the greater part of its sulfur by thorough stirring and moderate supply of air, but without external heating. (3) The nearly desulfurized blende must be brought in contact, at a temperature which does not exceed 800° , and with energetic stirring with a strong current of air, but without cooling.

Various special furnaces and processes for roasting blende have been described.² The separation of flue dust from blende gases has also been the subject of numerous patents;³ the use of the Cottrell electrostatic precipitator would seem to offer possibilities in this direction.

Many methods have been devised for the treatment of poor ores or mixed sulfide ores containing pyrites.⁴ The composition

1. W. Johnson, *Electrochem. and Metall. Ind.* 1905, **3**, 14; abst. J. S. C. I. 1905, **24**, 199. F. Thomas, *Metallurgie*, 1910, **7**, 610; abst. C. A. 1911, **5**, 265. V. Mostowitch, *Metallurgie*, **8**, 763; abst. C. A. 1912, **6**, 848. Hofmann, *Trans. Amer. Inst. Min. Eng.* 1904, 834. E. Jensch, *Zts. ang. Chem.* 1894, **7**, 50. V. Hassreidter, *Zts. ang. Chem.* 1906, **19**, 522. F. Doeltz and G. Graumann, *Chem. Zentr.* 1907, **78**, I, 1467. E. Prost, *Bull. Soc. Chim. Belg.* 1911, 103. M. Liebig, *Zink und Cadmium*, 1913, p. 222. C. Reed, U. S. P. 1069179. V. Mostowitch, *Zts. ang. Chem.* 1911, **24**, 763. A. Nemes, *Metallurgie*, 1912, 516; abst. *Zts. ang. Chem.* 1913, **26**, II, 55. W. Hommel, *Metallurgie*, 1912, 281.

2. C. de Saulles, U. S. P. 1183172, 1916. R. Zelewski, D. R. P. 195724. W. Buddeus, E. P. 29042, 1913. D. R. P. 278443. F. P. 466397. U. S. P. 1079897, 1121226. W. Borchers, R. Schenk and F. Thomas, D. R. P. 242312. W. Hommel, *Swiss P.* 72083. A. Queneau, U. S. P. 1132684. F. P. 445233. D. R. P. 288618. E. P. 15460, 1912.

3. G. Stone, U. S. P. 711187, 711188, 1902; abst. J. S. C. I. 1902, **21**, 1395. A. Hoffmann, *Metall u. Erz.* 1915, **12**, 290, 310. J. Lüttgens, D. R. P. 255535. Gräfflich von Landsberg-Velen und Gemensche Chemische Fabrik, D. R. P. 256237. Gewerkschaft Messel, Adolf Spiegel and Paul Meltzer, D. R. P. 260415. E. Liebrecht, D. R. P. 265584. F. Curtius & Co., D. R. P. Anm. C-23027. Metallbank und Metallurgische Gesellschaft A. G., F. P. 456524.

4. M. Hasenclever, J. S. C. I. 1911, **30**, 1291. T. Walker, E. P. 9918, 1909. A. Carmichael, D. R. P. 175426. G. Sweeting, F. P. 361808.

of burner gases from blende has been calculated by R. Hasenclever.¹

Sulfur Dioxide from Galena. The proposal to utilize the sulfur dioxide evolved in the smelting of galena was made by E. Hills, in 1857,² and has been made the subject of later patents.³ A dilute gas is thus obtained, and it is proposed to effect the denitration in the Glover tower by mixing these gases with more concentrated gas from the roasting of pyrites and blende.⁴ G. de Bechi⁵ converts lead and zinc sulfides in the ore into sulfates by treating the finely pulverized ore with a hot solution of ferric sulfate, containing free sulfuric and nitric acids: $\text{PbS} + \text{Fe}_2(\text{SO}_4)_3 = \text{PbSO}_4 + 2\text{FeSO}_4 + \text{S}$, the ferrous sulfate being converted into ferric sulfate by nitric acid. This process appears unduly expensive.

The reactions occurring in the roasting of lead sulfide have

A. Schillot, E. P. 21616, 1898. T. Huntington and F. Heberlein, E. P. 8064, 1896; 3795, 1897. J. Jones, U. S. P. 872822. O. Niedenführ, D. R. P. Ann. N-10069. J. Channing and F. Falding, U. S. P. 962498. P. Hart, J. S. C. I. 1895, **14**, 544. Maschinenbauanstalt Humboldt, D. R. P. 160694, 161151.

1. Chem. Ind. 1884, **7**, 79. In this connection see also: L. Bradford, E. P. 21880, 1914; abst. J. S. C. I. 1915, **34**, 1256. C. Crockford, E. P. 2647, 1860; 3117, 1866. G. and A. Davis, E. P. 2089, 1900. Erzverwertungs-Ges. m. b. H., E. P. 474306, 1914; abst. J. S. C. I. 1915, **34**, 803. P. Ferrere, E. P. 459371, 1912. P. Hart, E. P. 2000, 1891. Haviland, E. P. Appl. 86, 1916; E. P. 104516; abst. J. S. C. I. 1917, **36**, 29. A. Holdsworth, E. P. 25574, 1906. The D. E. Syndicate Ltd., E. P. 386634, 1908; abst. J. S. C. I. 1908, **27**, 690. A. Imbert, E. P. 12591, 12592, 1907; abst. J. S. C. I. 1908, **27**, 339. U. S. P. 875578, 1907; E. P. 10303, 1906; abst. J. S. C. I. 1906, **25**, 933; 1908, **27**, 129. H. Kirkpatrick-Picard, E. P. 22570, 1900; abst. J. S. C. I. 1902, **21**, 121. O. Kowalke, Amer. Electrochem. Soc. 1908, April-May. Electrochem. and Metall. Ind. 1908, **6**, 241; abst. J. S. C. I. 1908, **27**, 752. R. Liebig, D. R. P. 237034, 1910; abst. J. S. C. I. 1911, **30**, 1122. L. Letrange, E. P. 3211, 1881. W. Martin, E. P. 19449, 1910; abst. J. S. C. I. 1911, **30**, 1219. J. Russell and W. Hutton, E. P. 794, 1872. C. Rogers and A. Oswald, E. P. 21097, 1901; abst. J. S. C. I. 1902, **21**, 124. C. Sprague, U. S. P. 992391, 1911; abst. J. S. C. I. 1911, **30**, 753. E. Vuigner, E. P. 381038, 381039, 1906; abst. J. S. C. I. 1908, **27**, 129. L. Wright, J. S. C. I. 1914, **33**, 111. W. Swart, U. S. P. 882217; abst. J. S. C. I. 1908, **27**, 409.

2. E. P. 3091, 1857.

3. A. Nemes, E. P. 426851. C. Renwick, U. S. P. 981880. Grünewald & Welsch, D. R. P. 232014, 238293. Akt. Ges. f. Bergbau, Blei u. Zink Fabrikation zu Stolberg, D. R. P. 253492. Soc. Anon. d. Mines des Bormettes and A. Lotti, E. P. 346527, 1904; abst. J. S. C. I. 1905, **24**, 200. J. Gitsham, U. S. P. 1201955, 1916. E. P. 5299, 1915; abst. J. S. C. I. 1916, **35**, 698, 1218.

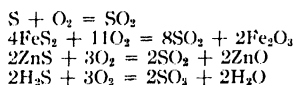
4. Akt. Ges. f. Bergbau, Blei u. Zink Fabrikation, D. R. P. 253493, 1911; abst. C. A. 1913, **7**, 687. Cf. E. Harworth, U. S. P. 268793; abst. J. S. C. I. 1883, **2**, 41.

5. G. de Bechi, E. P. 9939, 1906; 4246, 1913; abst. C. A. 1914, **8**, 2668; J. S. C. I. 1913, **32**, 540.

been discussed by F. Dempwolff,¹ W. Reinders,² and by C. Bannister.³ On heating to 450° lead sulfate is principally formed. At higher temperatures SO₂ is evolved, but no SO₃ until all the lead is converted into sulfate. At this stage mixtures of SO₂ and SO₃ in varying proportions are formed, until at 760° the ratio is SO₂:SO₃::65:35. At higher temperatures reduction sets in.

The Composition of Burner Gases. The gases from pyrites or blende burners, if intended for utilization in the contact process, will require careful purification.⁴ For the chamber process, only dust is removed.

The chemical reactions taking place in the production of sulfur dioxide by the various technical processes are as follows:



From these equations, and bearing in mind the fact that the air contains 23% (by weight) 20.9% by volume of oxygen, and 77% (by weight), 79.1% by volume of nitrogen (argon, etc.), the composition of any burner gas may be calculated when the amount of air used, and the percentage of sulfur burnt in the ore are known. In practice, however, it is necessary to take account of the sulfur trioxide always formed in burner gas, especially from pyrites burners from contact with the iron oxide which acts as catalyst.⁵ This usually amounts to about 15% or more of the total sulfur

1. Metall u. Erz, 1914, 619; Chem. Ztg. Rep. 1915, **39**, 127.
2. Zts. anorg. Chem. 1915, **93**, 213; abst. J. S. C. I. 1916, **35**, 847.
3. Inst. Min. Metall. 1912, Feb. 8th; abst. J. S. C. I. 1912, **31**, 285. See also A. Boulton, E. P. 2861, 1905. India P. Appl. 333, 1906. L. Bradford, E. P. 19844, 1914; abst. J. S. C. I. 1915, **34**, 182. D. Fitz-Gerald, E. P. 2481, 1875. J. Liardet and T. Donnithorne, E. P. 120, 1882.
4. I. Löhme, U. S. P. 1103522; abst. C. A. 1914, **8**, 3102; Zts. ang. Chem. 1916, **29**, I, 116; Mon. Sci. 1914, **81**, 178. Metallbank und Metallurgische Ges., F. P. 456524; abst. C. A. 1914, **8**, 1860; Chem. Ztg. Rep. 1914, **38**, 51. J. Herreshoff and General Chemical Co., U. S. P. 940945, 1113437; abst. C. A. 1914, **8**, 3842. E. Möller, D. R. P. 270757; abst. C. A. 1914, **8**, 2232; Zts. ang. Chem. 1914, **27**, 220; Chem. Ztg. Rep. 1914, **38**, 159; Wag. Jahr. 1914, **60**, I, 422.
5. Plattner, Die metallurgischen Röstprocesse. Fortmann, Dingl. Poly. 1868, **187**, 155. Scheurer-Kestner, Bull. Soc. Chim. 1875, **23**, 437; 1886, **45**, 227; abst. J. S. C. I. 1886, **5**, 324. F. Bode and Scheurer-Kestner, Dingl. Poly. 1875, **218**, 325; 1876, **219**, 512. G. Lunge and F. Salathe, Ber. 1877, **10**, 1824. G. Lunge, Chem. Ztg. 1883, **7**, 29. W. Hempel, Ber. 1890, **23**, 1455. Scheurer-Kestner, Bull. Soc. Chim. 1885, **43**, 9; **44**, 98. F. Fischer, Dingl. Poly. 1885, **258**, 28. Cf. Ber. 1874, **7**, 1665. E. Collett and M. Rickardt, Norw. P. 20273. Belg. P. 231311, 1910.

in pyrites gas, the gases from blende usually containing more. In practice, brimstone gas usually contains 10%-11% by volume of SO₂, and pyrites gas 7%-8%.¹

The composition of the burner gas and the amount of oxygen in the exit gas from the chambers are usually determined. The amount of sulfur dioxide may be estimated by Reich's method,² consisting in inserting in the burner flue a tube, through which gas is slowly aspirated into a solution containing 10 cc. N/10 iodine solution in 50 cc. water, together with a little starch and sodium bicarbonate until the color is discharged. The volume of the water used, plus 11.73 cc. for the SO₂ absorbed by 10 cc. N/10 iodine, gives the volume of burner gas. If the process is conducted as far as the total discharge of the color as is usual, the result is always too low, as some SO₂ escapes absorption in the last stages. It is more accurate, but less rapid, to titrate back the excess of iodine. The absorption bottle is about 200 cc. capacity, fitted with a double-hole rubber stopper, the inlet tube reaching to within 1/4 in. of the bottom, and drawn out to a fine point. The other tube is connected with the aspirator. At the end of the absorption the rate of gas should be very slow, and the end-point a faint lavender tinge. Rapid bubbling gives inaccurate results. The reaction is: $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$. The inaccuracy is caused by the presence of nitrogen oxides in the gases if the test is made after the niter-pots, and is small; but a little sodium acetate solution may be added to the absorption mixture when such gases are tested.³ This method gives only the SO₂ contained in the gas, and takes no account of the SO₃, usually present in appreciable amounts. For the purpose of estimating the total acidity of the gases, G. Lunge⁴ aspirated through 10 cc. N/10 NaOH, diluted with water to 100-200 cc. and colored with phenolphthalein. The gas is aspirated slowly with continuous shaking, as in the Reich test, until the color is discharged.

• The oxygen in the burner gas is not usually determined, although this is done with the exit gas. The estimation may be made in the usual way with alkaline pyrogallol in an Orsat or

1. W. Crowder, J. S. C. I. 1891, **10**, 298.

2. J. S. C. I. 1890, **9**, 1014.

3. F. Raschig, Zts. ang. Chem. 1909, **22**, 1182.

4. J. S. C. I. 1890, **9**, 1014.

other similar apparatus. The reagent consists of 10 gm. pyrogallol and 25 gm. stick potash in 400 cc. water. Phosphorus may be used if the temperature is kept above 16°, and half an hour allowed for the absorption. It is possible to estimate the SO₂ and oxides of nitrogen in a gas simultaneously.¹

Sulfur Dioxide from Sulfates. Attempts have been made to obtain sulfur dioxide for the manufacture of sulfuric acid from cheap metallic sulfates such as gypsum. L. Basset² mixes gypsum with clay and coal and treats with superheated steam at 900° in an oxidizing atmosphere to obtain sulfur dioxide and cement. Nearly all the processes aim at the simultaneous production of cement. F. Meyer³ heats a mixture of gypsum, silica and pyrites, the latter being added in such amount as to provide, on combustion, the heat necessary for the reaction between the gypsum and silica. A. Bambach⁴ heats the sulfate to redness in contact with a burning mixture of gas and air, an excess of oxygen being used, or first with a reducing flame and then with air, the process being also applicable to sulfides. R. Wedekind & Co.⁵ claim the same process as described by F. Meyer. F. Stanes and G. Roge⁶ heat sulfur with sodium or other acid sulfate in absence of free oxygen, the residue of monosulfite being converted into bisulfite by SO₂. L. Nonnet⁷ adds 5% gum arabic to a mixture of equal parts of alkali bisulfite and sodium thiosulfate which has been fused in its water of crystallization, and granulates the mixture. The granules evolve SO₂ in contact with water. J. Kiermayer⁸ reduces crude potassium salts containing magnesium sulfate by fusing with coke, a mixture of carbon dioxide and sulfur dioxide being evolved.

Other Sources of Sulfur Dioxide, besides those already considered include, as the most important, the spent oxide of iron

1. G. Lunge and P. Naef, *Chem. Ind.* 1884, **7**, 5.
2. E. P. 12027, 1912; 17873, 1913; 15612, 1913. F. P. 428019, 1910. U. S. P. 1168046, 1916; abst. C. A. 1912, **6**, 2148; J. S. C. I. 1913, **32**, 1012; 1916, **35**, 256.
3. U. S. P. 1008847; abst. C. A. 1912, **6**, 277.
4. F. P. 470652, 1914; abst. J. S. C. I. 1915, **34**, 282. E. P. 3174, 1914; abst. J. S. C. I. 1915, **34**, 905. D. R. P. Ann. P-30692.
5. E. P. 20186, 1910; abst. C. A. 1911, **5**, 2920; J. S. C. I. 1911, **30**, 362.
6. E. P. 18605, 1914; abst. J. S. C. I. 1915, **34**, 961; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 113.
7. E. P. 26999, 1912; F. P. 450804, 1912; abst. J. S. C. I. 1913, **32**, 602, 977. See also R. Tuson, E. P. 5159, 1878.
8. D. R. P. 312775, 1916; abst. J. S. C. I. 1919, **38**, 901-A.

mass used in the purification of coal-gas. • This material (p. 1031) is generally washed to separate ammonium salts, and frequently treated for the recovery of ferrocyanides and thiocyanates contained therein. The residue then consists of ferric oxide, with varying amounts of free sulfur, the maximum amount being about 50%. This oxide is now usually burnt in rotary mechanical furnaces of the Herreshoff type, but gives a very dusty gas which requires efficient dust separators. It has been stated that when spent-oxide is used for the manufacture of chamber acid, an additional amount of niter is required on account of the tarry matters contained in it which require oxidation. This ought not to be the case, as all tarry matter should be completely oxidized in the burners, and not allowed to pass over to the chambers. This is easy to ensure with proper regulation of air-supply. Proposals to extract the tar before burning¹ are therefore unnecessary. It should be mentioned that calcium carbonate is often present in the spent-oxide, and that this retains a portion of the sulfur as calcium sulfate, causing loss. This must be taken into consideration in analyzing the oxide. In the so-called "direct process" of K. Burkheiser,² it has been attempted to recover the sulfur of coal-gas as ammonium sulfate, but does not seem to have been successful.

Another source of sulfur dioxide is the alkali-waste of the Leblanc process, which is usually treated first to recover hydrogen sulfide by the method of Chance, and the gas then treated by the Claus process to recover sulfur (p. 1029), which is burnt in the ordinary way. Proposals to burn the hydrogen sulfide directly to sulfur dioxide in burners have not been adopted to any extent,³ the general opinion being that it is less expensive to separate the sulfur first by the Claus process. The burners are of simple type, consisting of a jet for the supply of gas, with apertures for the admission of air, and a brick chamber

1. B. Newlands, E. P. 596, 1868.
2. D. R. P. 217315, 1908; abst. C. A. 1910, **4**, 1531; Wag. Jahr. 1910, **56**, I, 41; Chem. Zentr. 1910, **81**, I, 490; Chem. Ztg. Rep. 1910, **34**, 19; Zts. ang. Chem. 1910, **23**, 474; Jahr. Chem. 1909, **62**, I, 626; Chem. Zts. 1910, **9**, No. 1758.
3. E. Lombard, Mon. Sci. 1889, **34**, 1231. J. Simpson and E. Parnell, E. P. 14711, 1886. R. Barth, D. R. P. 235157; abst. C. A. 1911, **5**, 3148; Zts. ang. Chem. 1911, **24**, 1445; Chem. Zentr. 1911, **82**, II, 118; Chem. Ztg. Rep. 1911, **35**, 338; Wag. Jahr. 1911, **57**, I, 433.

with baffle walls in which the combustion occurs. It might be possible to improve the process by using some type of Bunsen burner, with pre-heating of the gases.

Proposals to extract the sulfur dioxide from smoke and fire-gases¹ probably have in mind more to render the gases innocuous prior to their discharge into the atmosphere; they are hardly worthy of serious consideration as a source of SO₂.

The methods of treating waste sulfite cellulose liquors, and the recovery of the sulfur, have formed the subject of many

1. D. Peniakoff, E. P. 21476, 1912; abst. J. S. C. I. 1913, **32**, 424. U. Wedge, U. S. P. 1039464; abst. C. A. 1912, **6**, 3499; Chem. Ztg. Rep. 1913, **37**, 32. K. Takeda, E. P. 7272, 1913; abst. J. S. C. I. 1914, **33**, 360; Chem. Ztg. Rep. 1915, **39**, 55. Cie. Indust. des Alcools de l'Ardeche, E. P. 9145, 1909; abst. C. A. 1910, **4**, 653. Belg. P. 215493, 1909. Swiss P. 47574, 1909. F. Eustis, U. S. P. 1212199, 1917; 1265892, 1265893, 1918; abst. J. S. C. I. 1917, **36**, 389; 1918, **37**, 414-A; C. A. 1918, **12**, 1690. H. Kühne, E. P. 17520, 1908; abst. C. A. 1910, **4**, 652. Australian P. 12637, 1908. S. Osborn, et al., E. P. 6461, 1909; abst. C. A. 1911, **5**, 162. D. Peniakoff, E. P. 21476, 1912. F. P. 459926. W. Ramsay, E. P. 1427, 1883. K. Schnabel, E. P. 1893, 1881. A. Scott and A. Meyer, E. P. 439258, 1912; abst. J. S. C. I. 1912, **31**, 722. W. Thorp, E. P. 8862, 1889. U. Wedge, U. S. P. 1046915; abst. C. A. 1913, **7**, 685. U. Wedge and F. Eustis, U. S. P. 1260492; abst. C. A. 1918, **12**, 1499. H. Wislicenus, E. P. 16609, 1908. U. S. P. 988920. D. R. P. 228922, 229070. Swiss P. 44774. F. P. 397953. Belg. P. 212930. Norw. P. 19003. Aust. P. 45391. See also "Ueber die Abgasfrage," 1912. S. Young, U. S. P. 1262295; abst. C. A. 1918, **12**, 1588. See also J. Garner, U. S. P. 1145579. J. Garner and H. Clayton, U. S. P. 1173566. See also U. S. P. Re-14277, 1917. T. Murray and E. Ricketts, U. S. P. 1132679. Reuss, Rauch und Staub, 1914, 162. Bicke, Rauch und Staub, 1913, 162. Rippert, Glückauf, 1912, 1992, 2026. I. Moscicki, D. R. P. 256595. H. Falsche, D. R. P. 271786. H. Zschocke, D. R. P. 282088. R. Hasenclever, D. R. P. 17371; Wag. Jahr. 1881, **27**, 173. Wislicenus and Isachsen, D. R. P. 124900. O. Schott, Dingl. Poly. 1876, **221**, 142. Thirion, F. P. Feb. 28, 1874. C. Hering, "Die Verdichtung des Hüttenrauches," 1888. Schnabel, Metallhüttenkunde, ii, p. 58. E. Haworth, U. S. P. 268793, 1882. M. Freytag, D. R. P. 9969, 14928, 15546. J. Babe and H. Pape, D. R. P. 187381; E. P. 19973, 1906; Belg. P. 202371, 1907. H. Howard, U. S. P. 889132. F. Borchers, Chem. Zentr. 1909, **80**, II, 1177. V. Drewsen, U. S. P. 492196, 981625. J. Edmunds, E. P. 8006, 1910. H. Burbury, F. P. 420596, 1910, and addition 13752, 1911. Rayner and Crookes, E. P. 2678, 1875. Bernoulli, Wag. Jahr. 1880, **26**, 184. R. Hasenclever, D. R. P. 10710. E. Jensch, Wag. Jahr. 1889, **35**, 321. H. Spitta, D. R. P. 110388. Egestorff's Salzwärke, D. R. P. 70396. C. Winkler, D. R. P. 7174. R. Carpenter, 36th Alkali Rept., 1899, 25, 26. H. Precht, E. P. 3443, 1881. M. Lyte, J. S. C. I. 1882, **1**, 165. Schnabel, Wag. Jahr. 1882, **28**, 266. D. R. P. 16860. E. P. 5416, 1881. T. Fleitmann, D. R. P. 17397. C. Winkler, D. R. P. 14425. W. Thorp, E. P. 8862, 1889. R. Rössler, Dingl. Poly. 1881, **242**, 278; abst. Wag. Jahr. 1881, **27**, 184. D. R. P. 22850. G. Friese, Chem. Ind. 1895, **18**, 137. Landsberg, D. R. P. 6364. C. Winkler, Wag. Jahr. 1880, **26**, 245; Chem. Ind. 1880, **3**, 126. Kosmann, Wag. Jahr. 1882, **28**, 270. A. Allen, E. P. 189, 1879. Vivian, "Proceedings of the Subscribers to the Fund for obviating the inconvenience arising from the Smoke produced by smelting Copper Ores," London, 1833. M. Schroeder and E. Haenisch, D. R. P. 33100, 361761. L. Bœnelmans, D. R. P. 77335.

recent patents.¹ The different types of arrangement comprize (1) those in which the blow-off gases and liquor are taken off together, cooled, and conducted into the absorption plant, which is full of liquor; (2) those which are discharged from the digesters separately from the gases; (3) and those where the separation of the gas and liquid is effected in a special vessel outside the digester.

Preparation of sulfur dioxide from niter-cake,² petroleum acid-sludge,³ sewage,⁴ carbon disulfide,⁵ metallic oxides and sulfides in the electric furnace,⁶ have been described.

A solution of sulfurous acid may be obtained by treating a solution of calcium or sodium bisulfite with oxalic acid,⁷ but is more conveniently prepared by the absorption of the gas, as will subsequently be described.

For the preparation of bisulfites, see E. Carey and E. Hurter,⁸ and on the electrolytic oxidation of sulfurous acid consult M. and N. Thompson.^{9, 10}

Absorption of Sulfur Dioxide. Reference has been made in

1. H. Achenbach, D. R. P. 252412. W. Dickerson, U. S. P. 1059716, 1913; abst. J. S. C. I. 1913, **32**, 531. A. Kuhn, *Wochenbl. Papierfabr.* 1916, 2139, 2179, 2233, 2270; *Chem. Ztg. Rep.* 1917, **41**, 148; abst. J. S. C. I. 1917, **36**, 639. M. Platsch, E. P. 19600, 1912. A. Richter and L. Dunbar, U. S. P. 1213414, 1213415, 1917; abst. J. S. C. I. 1917, **36**, 334. A. Stutzer, *Chem. Ztg.* 1910, **29**, 1370. N. Hodgkins, U. S. P. 678179, 1901. A. Kummiller and E. Schultgen, D. R. P. 81338, 83438; abst. *Wag. Jahr.* 1895, **41**, 1027; *Zts. ang. Chem.* 1895, **8**, 395; 1896, **9**, 25. F. Kudelsky, D. R. P. 23586; abst. *Wag. Jahr.* 1883, **29**, 272.
2. *Chem. Fabrik Grünau, Landshoff & Meyer, A.-G.*, E. P. 6898, 1904; abst. J. S. C. I. 1905, **24**, 196; *J. Soc. Dyers Col.* 1905, **21**, 113. W. Garroway, E. P. 12986, 1905; abst. J. S. C. I. 1906, **25**, 536. H. Elworthy and D. Lange, F. P. 352254; abst. *Chem. Zts.* 1905, **4**, 376; *Mon. Sci.* 1906, **65**, 103.
3. G. Schildhaus and C. Condrea, U. S. P. 956184; abst. *Chem. Ztg. Rep.* 1910, **34**, 331; *Mon. Sci.* 1910, **73**, 129. J. and A. Blowski, U. S. P. 1010221. E. Southby, E. P. 1909, 1868.
4. E. Hills and B. Biggs, E. P. 3464, 1872.
5. J. Harvey, E. P. 4624, 1876.
6. M. Ruthenburg, E. P. 28126, 1910; abst. J. S. C. I. 1912, **31**, 646. C. d'Ogny, E. P. 16523, 1914.
7. F. Bond, E. P. 2247, 1877.
8. E. P. 5412, 1882.
9. *Met. Chem. Eng.* 1916, **15**, 677; abst. J. S. C. I. 1917, **36**, 81.
10. For other methods of obtaining SO₂, consult: H. Burbury, E. P. 2140, 1912; abst. C. A. 1913, **7**, 2456. L. Descamps, E. P. 100939, 1916; abst. J. S. C. I. 1916, **35**, 963. P. Contamin, U. S. P. 996215; abst. C. A. 1911, **5**, 2706. J. Garner and H. Clayton, U. S. P. 1173566, 1916; abst. J. S. C. I. 1917, **36**, 504. L. Nonnet, F. P. 450804, 1912; abst. J. S. C. I. 1913, **32**, 602. The Thiogen Co., F. P. 450786, 1912; abst. J. S. C. I. 1913, **32**, 602. E. P. 568, 1867; 469, 1869; 1770, 1870; 3760, 1873; 185, 2893, 1874; 1773, 4751, 1876; 215, 356, 1878; 2006, 1879; 5416, 5574, 1881; 955, 1167, 1665, 2930, 3607, 6064, 1882; 8912, 1885; 20494, 1909; 21476, 26999, 1912.

the preceding section to the methods of absorbing sulfur dioxide from smoke and other dilute gases. If a concentrated solution of SO_2 gas is required (liquid sulfurous acid), it is most readily prepared in ordinary absorption towers.¹ Absorption under pressure,² in apparatus with water-sprays,³ and in alcohol,⁴ have been proposed.

A special absorption tower devised by E. Hänisch and M. Schroeder⁵ utilizes the mixtures of sulfur dioxide and steam given off during the heating of a dilute solution of SO_2 , and acts as a rectifier. The mixture of gases enters the base of a lead tower, the lower half of which is filled with plates, the upper part containing coke. A fine spray of cold water falls from the top of the tower in such quantity that it just serves to condense the water vapor, which gives up its heat to the condensed water and maintains its temperature at about 100° . At this temperature the water can retain only 0.1%–0.5% SO_2 , and almost pure water collects at the bottom of the tower, while sulfur dioxide containing the minimum amount of moisture passes out of the top of the tower and is dried

1. J. Partington and L. Parker, *J. S. C. I.* 1919, **38**, 75. H. Howard, *U. S. P.* 889132, 1908; abst. *J. S. C. I.* 1908, **27**, 685. F. Coombs, *U. S. P.* 1147376; abst. *Chem. Ztg. Rep.* 1916, **40**, 146. J. Edmunds, *E. P.* 8006, 1910; abst. *J. S. C. I.* 1911, **30**, 85. F. Carpenter, *U. S. P.* 829765, 1906; abst. *Chem. Ztg. Rep.* 1906, **30**, 352; *Mon. Sci.* 1907, **67**, 152. M. Hatschek, *U. S. P.* 101011, 1870. W. Holzhäuser, *D. R. P.* 49194; abst. *Wag. Jahr.* 1889, **35**, 363. W. Jones, *U. S. P.* 185640, 1876; 188801, 197474, 1877. A. Reynoso, *U. S. P.* 185964, 1877. H. Moore and G. Richter, *U. S. P.* 1315189, 1919. E. Ritter and C. Kellner, *U. S. P.* 338557, 338558, 1886. F. Randon, *U. S. P.* 337197; abst. *J. A. C. S.* 1886, **8**, 68. J. Klinghammer, *D. R. P.* 6389; abst. *J. A. C. S.* 1879, **1**, 456. Norddeutsche Hütte A.-G. and Behrens, *E. P.* 134555; abst. *J. S. C. I.* 1919, **38**, 932-A. E. Espenhahn, *U. S. P.* 1315183, 1919; *E. P.* 134943, 1918; abst. *J. S. C. I.* 1919, **38**, 818-A; 1920, **39**, 23-A. *E. P.* 134943, 1920. E. Collett, *Norw. P.* 22807; abst. *Chem. Ztg.* 1913, **37**, 44. W. Feld, *Gasabteilung*, G. m. b. H., *D. R. P.* 314627; abst. *J. S. C. I.* 1920, **39**, 109-A. See also *D. R. P. Ann. F.* 33072; abst. *Chem. Ztg.* 1913, **37**, 326.
2. H. Frasch, *U. S. P.* 715778, 1902; abst. *J. S. C. I.* 1903, **22**, 93.
3. H. Burbury, *E. P.* 2140, 1912. *E. P.* 420506, 1910, and addition of Jan. 27, 1911; abst. *J. S. C. I.* 1911, **30**, 1012; 1913, **32**, 234. Cf. *E. P.* 2668, 1870; 667, 1874; 6461, 1909; 8006, 1910; F. Carlisle, *U. S. P.* 284817, 1883. M. Griffin, *Paper*, **21**, 64.
4. M. Kaltenbach, *U. S. P.* 1260681; abst. *C. A.* 1918, **12**, 1499; *J. S. C. I.* 1918, **37**, 302-A; *Mon. Sci.* 1918, **85**, 47.
5. *U. S. P.* 376883, 1888; 410415, 1889; abst. *J. A. C. S.* 1888, **10**, 49. See also W. Gossage, *E. P.* 3700, 1869. T. Webb, *E. P.* 1515, 1901; abst. *J. S. C. I.* 1902, **21**, 253. P. Marcelin and E. Ende, *U. S. P.* 28678, 1860. P. Marcelin, *U. S. P.* 123713, 1872. I. McDougall, *U. S. P.* 311595, 1885; abst. *J. A. C. S.* 1885, **7**, 67; *Wag. Jahr.* 1885, **31**, 208. W. Maynard, *U. S. P.* 180901, 1876.

by means of sulfuric acid of at least ninety per cent. concentration.

The absorption of sulfur dioxide in dicalcium phosphate has been advocated:¹ $2\text{CaHPO}_4 + 2\text{SO}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{Ca}(\text{HSO}_3)_2$. On heating the product to 100° all the sulfur dioxide is expelled, and dicalcium phosphate regenerated.

Gas masks for use in atmospheres containing sulfur dioxide have been described by A. Fieldner and S. Katz.² They recommend a standard army gas mask, the canister of which is charged with soda lime and cotton wadding.

Purification of Sulfur Dioxide. As obtained from brimstone and pyrites burners, sulfur dioxide contains many impurities. The gas from brimstone usually contains little besides sulfur trioxide (both gases, of course, being diluted with nitrogen), but when the brimstone contains arsenic or selenium, oxides of these elements may be present in the burner gas. If the gas is employed for the manufacture of chamber acid the presence of these impurities is of no consequence, but if used in the contact process it must be carefully purified. Pyrites gas, on the other hand, is contaminated with various impurities, and contains in addition a considerable amount of dust, chiefly iron oxide mechanically carried over from the kilns. This dust is present in large amounts if mechanical burners working with pyrites smalls or spent-oxide, are employed, and methods are necessary to remove it before the gas passes to the chamber plant. The pyrites gas also nearly always contains arsenic, frequently small amounts of selenium and thallium, and other substances, which are not usually removed by special means in connection with the chamber process but must be rigorously separated if the gas is to be treated by the contact process.

The separation of the following impurities from burner gas is considered herein.

- (1) Dust, mechanically carried over.
- (2) Sulfur trioxide and sulfuric acid fog.
- (3) Arsenic and other impurities.

Dust is separable from burner gas by passage through flues

1. D. R. P. 160940; abst. Chem. Centr. 1905, **76**, II, 89; Jahr. Chem. 1905-1908, I, 1557; Chem. Zts. 1906, **5**, 386; Chem. Ztg. 1905, **29**, 620; Wag. Jahr. 1905, **51**, I, 392. See also E. Espenhahn, U. S. P. 1315183, 1919; abst. J. S. C. I. 1919, **38**, 818-A.

2. Chem. Met. Eng. 1919, **20**, 582.

and chambers, usually of brickwork, provided with baffles. The gas from mechanical burners requires a much more efficient dust-separator than that from hand-fired kilns, and for this purpose a brickwork chamber filled with broken bricks resting on bars is used. These bars are moved daily in order to let down a portion of the brickwork, which is replaced by fresh brickwork fed in at the top. Care must be exercised that the cooling surface presented to the gas is not excessive, or it may enter the Glover tower at too low a temperature. A considerable amount of dust is inevitably carried over to this tower, forming a mud or sludge in the acid.

The flues for conveying the burner gases may be of brickwork up to where there is a possibility of condensation of liquid acid from the gases, from which point they must be of cast-iron, or, if the temperature is low enough, of lead, the gases usually not being cooled where a Glover tower is used. The flue dust which collects must be removed periodically, as it soon hardens to a stonelike mass. Its composition is variable.¹

A centrifugal dust-catcher has been devised by F. Falding.² A magnetic separator has been described,³ but is probably not in use. Numerous special types of dust separators have from time to time been advocated, few of which appear to have been installed.⁴

The gases used for the manufacture of sulfite cellulose must

1. Bauer, *Jahr. f. Berg. u. Hüttenw.* 1894, 39. F. Bellingrodt, *Chem. Ztg.* 1886, **10**, 1039. E. Gibbon, *Chem. Trade J.* 1905, **36**, 88. G. Krause, *D. R. P.* 55676; *abst. Zts. ang. Chem.* 1891, **4**, 248; *Wag. Jahr.* 1891, **37**, 273; *Ber.* 1891, **24**, 604; *Mon. Sci.* 1891, **38**, 655. D. Playfair, *Chem. News*, 1879, **39**, 245. F. Reich, *J. prakt. Chem.* 1863, **90**, 176. C. Hering, "Die Verdichtung des Hüttenrauchs," 1888, 8. See also *Freiburger Jahrbuch*, 1879, 151.

2. F. Falding, *Min. Ind.* **9**, 623.

3. J. Morton and United Alkali Co., *E. P.* 17461, 1906; *abst. J. S. C. I.* 1907, **26**, 823.

4. A. Geyer, *D. R. P.* 227387; *abst. Wag. Jahr.* 1910, **56**, I, 628. C. Heine, *D. R. P.* 230182; *abst. Chem. Ztg. Rep.* 1911, **35**, 84. The Metallic Compounds Separation Syndicate, *D. R. P.* 153641. K. Krowatschek, *D. R. P. Ann. K-45381*, 1911; *abst. Zts. ang. Chem.* 1911, **24**, 2179. H. Howard, *U. S. P.* 896111 and Re-13090. *U. S. P.* 970053, 1910. E. Hartmann and F. Benker, *Zts. ang. Chem.* 1906, **19**, 1188. Maschinenfabriken Augsburg und Nürnberg, *D. R. P.* 169818. R. Scheibe, *D. R. P.* 184038; *abst. Chem. Ztg. Rep.* 1907, **31**, 264. C. Reese, *U. S. P.* 989801, 1911. F. Benker and E. Hartmann, *F. P.* 387456. Scherfenberg & Prager, *D. R. P.* 203948. J. Herreshoff, *U. S. P.* 940595, 940596, 955067, 969868. F. Brandenburg, *Zts. ang. Chem.* 1909, **22**, 2490. Wright, *Eng. Min. J.* 1910, 111. J. Shields, *E. P.* 16353, 16354, 1904. *D. R. P.* 180070, 180071. R. Cellarius, *E. P.* 22080, 1905. *Soc. Belg. Koerting, Belg. P.* 251637; *abst. Ztg.* 1913, **37**, 244.

be free from sulfuric acid, and this is accomplished by passing through coolers consisting of perpendicular cast-iron pipes, ending in a lead-lined pipe with a manhole.¹ Selenium is distinctly injurious.²

The separation of arsenic and fog from gases used in the contact process will be considered more in detail under that heading. It may be mentioned that filtration through porous bodies,³ treatment with a shower of dilute sulfuric acid,⁴ or nitrous vitriol,⁵ hot water in a washer,⁶ cold water in a tower,⁷ filtration through ferric sulfate⁸ or aluminium sulfate⁹ or charcoal,¹⁰ or exposure to electrical discharges when mixed with water vapor and nitrous gases¹¹ have been suggested.

In order to separate sulfuric acid mist it has been proposed to use dry air for the burners, when no sulfuric acid can be formed,¹² or to pass the gases over carbon at high temperatures, when the

1. Papierztg. 1894, 2099, 2130. E. Nemethy, D. R. P. 48285, 1889; abst. Wag. Jahr. 1889, **35**, 363. E. Collett and M. Eckardt, D. R. P. 244841; abst. Wag. Jahr. 1912, **58**, I, 373. T. Briggs, U. S. P. 1301372; abst. C. A. 1919, **13**, 1905.

2. P. Klason and H. Mellquist, Papierztg. 1912, 767. Swed. P. 35177, 1911; abst. C. A. 1914, **8**, 657. S. Young, E. P. 26482, 1912. R. Messel, U. S. P. 1078937. F. P. 414387, 1910; abst. J. S. C. I. 1910, **29**, 1203; 1913, **32**, 1156. Wright, Eng. Min. J. 1910, **90**, 111. E. Asbrand, D. R. P. 243787; abst. Chem. Zentr. 1912, **83**, I, 760. G. Pereulok, E. P. 12312, 1907; abst. C. A. 1908, **2**, 308. See also W. Beth, D. R. P. 245569; abst. C. A. 1912, **6**, 2344; Wag. Jahr. 1912, **58**, I, 486. K. Michaelis, D. R. P. 244206; abst. C. A. 1912, **6**, 2197; Wag. Jahr. 1912, **58**, I, 488. Maschinenfabrik Buckau, D. R. P. 245319.

3. F. Girod, E. P. 17157, 1911. J. Shields, D. R. P. 180071, 1904; abst. C. A. 1907, **1**, 1937. J. Tufts, U. S. P. 891115, 891116, 1908; abst. J. S. C. I. 1908, **27**, 750.

4. A. Düron, E. P. 9869, 1910; abst. C. A. 1911, **5**, 3133. C. Reese, U. S. P. 989801; abst. C. A. 1911, **5**, 2159. J. Herrshoff, U. S. P. 949595; abst. C. A. 1910, **4**, 499.

5. F. Girod, E. P. 17157, 1911; abst. C. A. 1913, **7**, 403; J. S. C. I. 1912, **31**, 687.

6. L. Basset, E. P. 20667, 1913; abst. Chem. Ztg. 1915, **39**, 147.

7. H. Hegeler, U. S. P. 931868; abst. C. A. 1909, **3**, 2619.

8. A. Düron and E. Hartmann, E. P. 9869, 1910; abst. C. A. 1911, **5**, 3133; J. S. C. I. 1911, **30**, 621. Belg. P. 226458, 1910.

9. F. Projahn, D. R. P. 221847; abst. Zts. ang. Chem. 1910, **23**, 1531; Chem. Zentr. 1910, **81**, I, 1904; Jahr. Chem. 1910, **63**, I, 616; Zts. Schiess. Spreng. 1910, **5**, 256; Chem. Ztg. Rep. 1910, **34**, 259; Wag. Jahr. 1910, **56**, I, 417; Mon. Sci. 1914, **81**, 76.

10. A. Allen, E. P. 189, 1879; abst. J. A. C. S. 1880, **2**, 71.

11. U. S. P. 1022012, 1912; abst. J. S. C. I. 1912, **31**, 489. See also Badische Anilin & Sodafabrik, D. R. P. 159976; abst. Wag. Jahr. 1905, **51**, I, 390.

12. H. Humphries, E. P. 10810, 1912; abst. J. S. C. I. 1913, **32**, 141.

sulfuric acid is reduced.¹ A combined apparatus has been described.²

The purification of burner gas from chlorine³ is necessary for the contact process; this is done by washing with milk of lime. Fluorine may be removed⁴ by treatment with sulfuric acid and nitrous vitriol.⁵

Liquid Sulfur Dioxide. For the preparation of liquid sulfur dioxide a pure gas is necessary. It may be best for this purpose to prepare the gas by a chemical process, such as the action of strong sulfuric acid on copper, carbon, sulfur, pyrites,⁶ by heating ferrous sulfate with sulfur,⁷ or by the purification of burner-gas.⁸

Liquid sulfur dioxide was first made on a large scale by R. Pictet,⁹ who employed it as a refrigerant. The best known process used in its manufacture is that of E. Haenisch and M. Schroeder,¹⁰ in use in Rhenish Prussia, Silesia and for a time at

1. R. Messel, E. P. 22672, 1909. D. R. P. 226331, 1909; abst. C. A. 1911, **5**, 1326, 2916; J. S. C. I. 1910, **29**, 1250; Zts. ang. Chem. 1910, **23**, 2098; Chem. Zentr. 1910, **81**, II, 1254; Jahr. Chem. 1910, **63**, I, 508; Chem. Ztg. Rep. 1910, **34**, 510; 1911, **35**, 3; Wag. Jahr. 1910, **56**, I, 418; Mon. Sci. 1914, **81**, 82, 87; Zts. Schiess. Spreng. 1910, **5**, 440.
2. Metallurgische Gesellschaft, Frankfurt, D. R. P. 161017; abst. Zts. ang. Chem. 1905, **18**, 1464; Chem. Centr. 1905, **76**, II, 90; Chem. Zts. 1906, **5**, 388; Chem. Ztg. 1905, **29**, 644; Wag. Jahr. 1905, **51**, I, 390. Tentelew Chemical Co., F. P. 431067.
3. Tentelew Chemical Co., D. R. P. 194176, 230585; abst. Zts. ang. Chem. 1908, **21**, 931; 1911, **24**, 425; Chem. Ztg. Rep. 1908, **32**, 94; 1911, **35**, 95; Wag. Jahr. 1908, **54**, I, 368.
4. H. Klencke, F. P. 408417; abst. Mon. Sci. 1911, **75**, 145.
5. Other processes are: J. Blanc, U. S. P. 1034574, 1912; abst. J. S. C. I. 1912, **31**, 815. Cie. Industrielle des Procédés R. Pictet, E. P. 3714, 1882. D. R. P. 22365; abst. Wag. Jahr. 1883, **29**, 268. H. Frasch, U. S. P. 715778, 1902; abst. J. S. C. I. 1903, **22**, 93. Badische Anilin und Sodafabrik, D. R. P. 287471. J. Herreshoff, U. S. P. 1113437. R. Cellarius, D. R. P. 263941. E. Illingsworth, E. P. 8218, 1912. A. McDougall, E. P. 145, 1872. U. Wedge and F. Eustis, U. S. P. 1260493; abst. C. A. 1918, **12**, 1499. See Exptl. Rep. No. 41, H. M. Factory, Gretna.
6. P. Hart, E. P. 13950, 1885; abst. Wag. Jahr. 1887, **33**, 497. See also A. Harpf, "Flüssiges Schwefeldioxyd," Stuttgart, 1900.
7. T. Terrell, E. P. 5930, 1884; abst. Wag. Jahr. 1884, **30**, 276; 1885, **31**, 310; J. S. C. I. 1834, **3**, 414.
8. E. Bergmann and T. Berliner, D. R. P. 160940; abst. Chem. Centr. 1905, **76**, II, 89. F. Carpenter, U. S. P. 829765; abst. Chem. Zts. 1906, **5**, 545; Chem. Ztg. Rep. 1906, **30**, 352; Mon. Sci. 1907, **67**, 152. P. Marin, F. P. 374519. H. Hegeler and L. Heinz, U. S. P. 931868; abst. Chem. Ztg. Rep. 1909, **33**, 531. M. Moulin and R. Vandoni, F. P. 432431. Cie. ind. des Alcools de l'Ardeche, E. P. 9145, 1909; abst. J. S. C. I. 1909, **28**, 1033. H. Ford, U. S. P. 363457; abst. J. A. C. S. 1887, **9**, 125; Wag. Jahr. 1887, **33**, 497.
9. E. P. 2727, 1875. D. R. P. 22365; abst. J. S. C. I. 1883, **2**, 413; Wag. Jahr. 1883, **29**, 268. U. S. P. 191778, 1877; 268530, 1882.
10. E. P. 2621, 1883; 6404, 6405, 1885; abst. J. S. C. I. 1885, **4**, 674; Chem. Ind. 1884, **7**, 120. Zts. ang. Chem. 1888, **1**, 488. D. R. P. 52025;

Bound Brook, N. J. The apparatus is somewhat complicated. The hot burner gas (which may contain as little as 6% passes beneath lead pans where it is cooled, and then to the washing tower packed with coke, down which cold water passes. All the SO_2 is absorbed, while the waste gases passing out into the air, contain but 0.05% SO_2 by volume. The solution contains about 1% SO_2 , and runs off by a pipe to the preheater, consisting of a number of superposed lead plates, forming shallow chambers $1\frac{1}{2}$ in. deep, in which hot spent liquor and cold solution pass in alternate sections at right angles. The cold acid is heated from 15° to 85° and the hot spent liquor is cooled from 95° to 25° . This latter runs to waste. This preheater has more recently been replaced by cylindrical coolers working on the same principle. The preheated acid now travels in succession through lead pans where it is heated to boiling by the burner gas, the vapors passing through a cooling worm and then to a drying tower containing coke moistened with strong sulfuric acid. The dry SO_2 next passes to a pump. The boiling liquor from the pans, still containing some SO_2 , passes a column where it is separated from the water vapor by the process described in the preceding section. The water condensed in the worm also passes to a column to be deprived of SO_2 , the hot spent liquor running off being utilized in preheating the cold acid. To regulate the compression of the SO_2 a large rubber bag is interposed between the pump and the rest of the plant. The compressed gas enters a worm and is liquefied by cooling and pressure, e. g., 1.26 atm. at 10° , 2.24 atm. at 20° , 3.51 atm. at 30° . From the worm the liquid SO_2 runs into a wrought-iron reservoir from which it is filled into iron bottles or into tank-wagons. The reservoir is provided with a blow-off valve to allow permanent gases to escape, these being sent back to the tower.

H. Niefenführ¹ liquefies the SO_2 directly without using an absorption process, by pressure and cooling by expansion.²

Commercial liquid sulfur dioxide is usually pure, but some-
 abst. Zts. ang. Chem. 1890, **3**, 414; Wag. Jahr. 1890, **36**, 1160; Ber. 1891, **23**, 511.

1. D. R. P. 254044, 254362; abst. C. A. 1913, **7**, 1085; J. S. C. I. 1913, **32**, 194, 232.

2. H. Niefenführ, D. R. P. 254044, 254362. H. Moore and R. Wolf, U. S. P. 1091689. J. Blanc, U. S. P. 1034574. H. Burbury, F. P. 420596. P. Pacottet, F. P. 365224. H. Humphries, E. P. 10810, 1912. L. Nonnet,

times contains sulfuric acid—according to Lunge, up to 20%. It is stored in iron cylinders or tank-wagons, or, in small amounts in glass siphon. The pressure of the saturated vapor at different temperatures is given in the following table (Regnault, 1862):

| | | | | | | | | | |
|-------------------|------|------|-----|------|------|------|------|------|------|
| Degree C. | -39 | 20 | 10 | 0 | +10 | 20 | 30 | 40 | 50 |
| Pressure atm. . . | 0.39 | 0.63 | 1.0 | 1.53 | 2.26 | 3.24 | 4.52 | 6.15 | 8.19 |

The bottles are not more than nine-tenths filled to allow for expansion, and should be tested to 50 atm.

Properties of Sulfur Dioxide. Sulfur dioxide at the ordinary temperature and pressure is a colorless gas, of suffocating smell, not combustible, nor does SO_2 support combustion. When present in but small amounts in the atmosphere it has an injurious action on animal and vegetable life. The poisonous effect of chimney gas and smeltery fumes on green plants is chiefly due to the presence of this gas,² which has a distinct germicidal action.³ The density of the gas has been found by various observers to be from 2.222 to 2.247 (air = 1); the density as found by Leduc is 2.9266 grams per liter at 0° and 760 mm. The coefficient of expansion is greater than that of air, especially at lower temperatures (Amagat); and according to the latter's investigations, and those of

E. P. 26999, 1912. F. P. 450804. L. Basset, E. P. 20667, 1913. M. Kaltenbach, F. P. 481846, 1917; abst. C. A. 1917, **11**, 3395. U. Wedge and F. Eustis, U. S. P. 1260492, 1260493, 1918; abst. J. S. C. I. 1918, **37**, 301-A. See Chem. Ztg. 1916, **40**, 80. J. Davenport, U. S. P. 1317688, 1919; abst. C. A. 1919, **13**, 3289.

1. A. Mather, D. R. P. 261506; abst. C. A. 1913, **7**, 3256; Zts. ang. Chem. 1913, **26**, 438; Wag. Jahr. 1913, **59**, I, 515. Heylands Co., D. R. P. 250263; abst. C. A. 1913, **7**, 6; Zts. ang. Chem. 1912, **25**, 2186; Wag. Jahr. 1912, **58**, I, 514. R. Meves, D. R. P. 292727; abst. Zts. ang. Chem. 1916, **29**, 365; Chem. Ztg. Rep. 1916, **40**, 284. See also E. Porat, U. S. P. 585404, 1897. D. R. P. 96157; abst. Wag. Jahr. 1898, **44**, 325; Chem. Centr. 1898, **69**, I, 1086.

2. R. Tatlock and R. Thomson, Chem. Trade J. 1914, 396; Analyst, 1914, **39**, 203; abst. C. A. 1914, **8**, 2559. For further information on the action of SO_2 on plant and animal life, see: M. Ogata, Arch. Hygiene, 1884, 223. F. Lehmann, Zts. ang. Chem. 1893, **6**, 612. M. Freytag, Wag. Jahr. 1873, **19**, 180. J. Schröder, Wag. Jahr. 1874, **20**, 277. A. Stöckhart, Wag. Jahr. 1874, **20**, 278. E. Fricke, Chem. Ind. 1887, **10**, 492. L. Just and H. Heine, Chem. Ind. 1889, **12**, 252. F. Fischer, Dingl. Poly. 1876, **220**, 88. Morren, Chem. Trade J. **2**, 188. J. König, Dingl. Poly. 1878, **229**, 299. R. Hasenclever, Chem. Ind. 1879, **2**, 225. S. Hamburger, J. S. C. I. 1884, **3**, 202. See A. Wieler, Einwirkung von Schwefliger Säure auf Pflanzen, 1905. Haselhof and Lindau, Die Beschädigung der Vegetation durch Rauch, 1903.

3. E. Hailer, Zts. ang. Chem. 1913, **26**, II, 589; Arb. Kais. Gesundh. **36**, 297; abst. C. A. 1911, **5**, 1805.

some of his contemporaries, the most probable results are as follows:

| | |
|------------|-----------|
| 0° to 10° | 0.004233 |
| 10° to 20° | 0.004105 |
| At 50° | 0.003846 |
| At 100° | 0.003757 |
| At 150° | 0.003718 |
| At 200° | 0.003695 |
| At 250° | 0.003685. |

The specific heat at ordinary temperature is 0.1544; E. Mathias¹ gives for this between -20° and 130° the formula:

$$s = 0.31712 \pm 0.0003507t + 0.000006762t^2 \text{ where } t = ^\circ\text{C.}$$

L. Cailletet and E. Mathias² have also determined the density of the saturated vapor.

The heat of formation from rhombic sulfur is, for 1 gm.-mol. (64.06 gm.) 71.08 kgm. cal. according to Thomsen, or 69.26 kgm. cal. according to Berthelot, both at constant pressure and volume.

The gas is readily liquefied, either by cooling to -10° at normal pressure,³ or by moderate pressure at atmospheric temperature (see p. 1092), forming a colorless solid at -76°. The latent-heat of the liquid has the following values:

| | | | | |
|--------------------------------|------|------|------|------|
| Temperature of evaporation, C. | 0 | 10 | 20 | 30 |
| Latent Heat, cal. | 91.2 | 88.7 | 84.7 | 80.5 |

The specific gravity of the liquid at 15° is 1.3964; its value at different temperatures having been determined by A. Lange.⁴ The liquid does not act on iron up to 100° if pure; technical liquid contains a little water and slightly corrodes iron. The temperature at which this occurs increases with the purity of the substance, and since the liquid cannot dissolve more than 1% of water, this action can never occur at the atmospheric temperature. The iron salts formed act as a protecting crust.

Sulfur dioxide is freely soluble in water, forming sulfurous acid which, however, has not been isolated in the pure state. The solution loses SO₂ on exposure to the air, and also takes up oxygen to form sulfuric acid,⁵ which oxidation is considerably retarded by the presence of glycerol. The solubility of SO₂,

1. Compt. rend. 1894, **119**, 404; abst. Jahr. Chem. 1894, **47**, 404.
2. Compt. rend. 1887, **104**, 1563; abst. Jahr. Chem. 1887, **40**, 74.
3. H. Gibbs, J. A. C. S. 1905, **27**, 851; abst. J. C. S. 1905, **88**, ii, 570.
4. Zts. ang. Chem. 1899, **12**, 275, 300, 595; abst. Jahr. Chem. 1899, **52**, 421.
5. P. Förster, Arb. d. Kaiserl. Gesundheitsamts, 1914, 468; Chem. Ztg. 1915, **39**, 447; abst. C. A. 1915, **9**, 1821.

under 760 mm. pressure, at other temperatures is given in the following table:¹

| Temp. C. | 1-Liter Water Dissolves Lit. SO ₂ | 1 Liter Water Dissolves Grams SO ₂ | Sp. Gr. Solution | Per cent. SO ₂ in Solution | 1 Liter Solution Contains Lit. SO ₂ |
|-------------|---|--|---------------------|---|---|
| 0 | 79.8 | 228.3 | 1.0609 | 18.58 | 68.86 |
| 5 | 57.5 | 193.1 | 1.059 | 16.19 | 59.82 |
| 10 | 56.6 | 161.9 | 1.0547 | 13.93 | 51.38 |
| 15 | 47.3 | 135.3 | 1.042 | 11.92 | 43.56 |
| 20 | 39.4 | 112.7 | 1.0239 | 10.12 | 36.21 |

The specific gravity of the solutions is given in Chapter VIII.

Sulfur dioxide is soluble in certain oils,² and to some extent in fused metals.³ At higher temperatures, in sealed tubes, the solution breaks up into sulfur and sulfuric acid, but hydrosulfurous acid is first formed:⁴ $3\text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{S}_2\text{O}_4 + \text{H}_2\text{SO}_4 = 2\text{H}_2\text{SO}_4 + \text{S}$.

A mixture of sulfur dioxide and oxygen, when submitted to the silent electric discharge, is said to form a higher oxide of sulfur, S_2O_7 . The electrolysis of the solution produces sulfuric acid at the anode.⁵

Sulfur dioxide oxidizes carbon monoxide at 1000° – 1200° : $2\text{CO} + \text{SO}_2 = 2\text{CO}_2 + \frac{1}{2}\text{S}_2$,⁶ traces of COS being formed.⁷

Analysis of Sulfur Dioxide. In the detection of sulfur dioxide the smell of the gas may be used, as it is characteristic and observable in quite small amounts. Sulfites are treated with

1. H. Sims, J. C. S. 1861, **14**, 376; Ann. 1861, **118**, 333; Zts. Chem. 1861, **4**, 376; abst. Chem. Centr. 1861, **32**, 690; Jahr. Chem. 1861, **14**, 54.

2. A. Guiselin, Mat. grasses, **6**, 3144; abst. C. A. 1913, **7**, 4048.

3. A. Sieverts and E. Bergner, Zts. physik. Chem. 1913, **82**, 257; abst. J. S. C. I. 1913, **32**, 257.

4. E. Jungfleisch and L. Brunel, Compt. rend. 1913, **156**, 1719; abst. J. S. C. I. 1913, **32**, 697.

5. M. Thompson and A. Sullivan, Met. Chem. Eng. 1918, **18**, 178; abst. J. S. C. I. 1918, **37**, 213-A.

6. J. Ferguson, J. A. C. S. 1918, **40**, 1626; abst. C. A. 1919, **13**, 11.

7. The photoelectric phenomena exhibited by liquid sulfur dioxide have been described by J. Carvallo, Compt. rend. 1913, **156**, 1882; abst. J. S. C. I. 1913, **32**, 750. See also C. Garrett, Phil. Mag. 1916, (6), **31**, 505, 512; abst. C. A. 1916, **10**, 2833. A. Ditte, Ann. Chim. Phys. 1907, (8), **12**, 229; abst. Chem. Zentr. 1908, **79**, 1, 799; J. S. C. I. 1908, **27**, 334. W. Henderson and H. Weiser, J. A. C. S. 1913, **35**, 239; abst. J. S. C. I. 1913, **32**, 361. The solubility of SO_2 in H_2SO_4 is discussed in Exptl. Rep. No. 57, H. M. Factory, Gretna.

dilute sulfuric acid, to liberate sulfur dioxide. A more sensitive test is the liberation of iodine from potassium iodate ($2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} = \text{I}_2 + 2\text{KHSO}_4 + 3\text{H}_2\text{SO}_4$). Paper soaked in a solution of potassium iodide and starch may be used (see p. 408), this being turned blue by traces of sulfur dioxide. If the latter is in excess, the paper is again bleached ($\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$). This reaction is used in the estimation of sulfurous acid or, after acidification, of sulfites. The solution is run from a burette into standard iodine solution, a little starch-paste being added when the color of the iodine has become very pale, and the titration continued until the blue color just disappears on shaking. The iodine should not be run into the sulfite solution, as then a side reaction occurs: $\text{SO}_2 + 4\text{HI} = 2\text{I}_2 + 2\text{H}_2\text{O} + \text{S}$. According to R. Bunsen,¹ an aqueous solution of sulfur dioxide can only be quantitatively oxidized to sulfuric acid by means of iodine if the proportion of SO_2 in solution does not exceed 0.04% to 0.05%.

In gravimetric analysis, sulfite is oxidized to sulfate by means of bromine or chlorine, which may then be precipitated by barium chloride. Since, however, sulfites usually contain sulfates, this method does not give accurate results unless the sulfate is first estimated, as by precipitation with barium chloride in acid solution (barium sulfite being soluble in acids).

A point of great importance in the estimation of sulfur dioxide or sulfites is the case with which these substances undergo oxidation in contact with air. According to A. Titoff,² this oxidation would probably not occur in perfectly pure water, but is so greatly accelerated by small amounts of copper and iron salts, that the minute traces of these often present in distilled water act as catalysts for the reaction: $2\text{H}_2\text{SO}_3 + \text{O}_2 = 2\text{H}_2\text{SO}_4$. One gm. copper per million liters is said to exert an appreciable influence. Oxidation is considerably retarded by the addition of glycerol, mannitol, etc., which probably form complex compounds with the catalytic metal ions.³

1. J. C. S. 1856, **9**, 219. See also Finkener, *Traite d'Analyse*, II, 937. R. Bunsen, *Ann.* 1853, **86**, 26.

2. *Zts. physik. Chem.* 1903, **45**, 611; abst. *Jahr. Chem.* 1903, **56**, 219.

3. F. Raschig, *Zts. ang. Chem.* 1904, **17**, 580. J. Baker and F. Day, *Analyst*, 1912, **37**, 439; abst. C. A. 1913, **7**, 663. W. Giles and A. Shearer, *J. S. C. I.* 1884, **3**, 197; 1885, **4**, 303. L. Andrews, *J. A. C. S.* 1903, **25**, 756. G. Jamieson, *Amer. J. Sci.* 1914, **38**, 166; abst. C. A. 1914, **8**, 3279.

P. Haller¹ applies the following reactions: In feebly acid solutions the relation between potassium iodate and iodide is: $5\text{KI} + \text{KIO}_3 + 6\text{HCl} = 6\text{KCl} + 3\text{H}_2\text{O} + 3\text{I}_2$. In solutions containing at least 15% to 20% HCl the reaction can proceed further with excess of iodate: $2\text{I}_2 + \text{KIO}_3 + 6\text{HCl} = \text{KCl} + 3\text{H}_2\text{O} + 5\text{ICl}$, the iodine monochloride being fairly stable in presence of excess of free acid. The reaction between iodide and iodate in strongly acid solution therefore becomes: $2\text{KI} + \text{KIO}_3 + 6\text{HCl} = 3\text{KCl} + 3\text{H}_2\text{O} + 3\text{ICl}$. The end point, when free iodine disappears, can be ascertained by adding a globule of chloroform, which is colored purple by the free iodine, but not by iodine monochloride. When sulfites are titrated, the reaction is: $2\text{SO}_2 + \text{KIO}_3 + 2\text{HCl} = 2\text{SO}_3 + \text{KCl} + \text{H}_2\text{O} + \text{ICl}$. Glycerol is added to prevent oxidation of the sulfite during the titration. This alcohol may also with advantage be added to caustic soda used to absorb SO_2 from gases in the analysis of the latter, about 5% by volume being sufficient. The acid solution of SO_2 is titrated with a standard solution of iodate, this being added till the color of the iodine disappears.

A test for SO_2 in gases has been disclosed by Denigès,² and the qualitative detection of sulfites, sulfides, sulfates and thio-sulfates together, by L. Dobbin.³ Iodometric methods of estimation have also been described by A. Fairlie,⁴ H. Ljungh,⁵ J. Ferguson,⁶ G. Jones, J. Capps and S. Katz,⁷ and G. Jamieson.⁸ Titration with alkali has been used by A. Sander,⁹ E. Kedesdy,¹⁰ and E. Bosshard and W. Grob,¹¹ and absorption in sodium carbonate and hydrogen peroxide by R. Nestell and E.

1. J. S. C. I. 1919, **38**, 52-T; abst. C. A. 1919, **13**, 1438. See also A. Abramski, D. R. P. 309981; abst. J. S. C. I. 1919, **38**, 361-A.

2. Bull. Soc. Pharm. Bordeaux, April, 1914. Ann. Chim. Analyt. 1915, **20**, 10; abst. J. S. C. I. 1915, **34**, 149.

3. Chem. and Druggist, 1903, **63**, 520; abst. J. S. C. I. 1903, **22**, 1148.

4. U. S. P. 1205724, 1916; abst. J. S. C. I. 1917, **36**, 83; Mon. Sci. 1917, **84**, 51.

5. Chem. Ztg. 1909, **33**, 143; abst. Jahr. Chem. 1909, **62**, I, 488; C. A. 1909, **3**, 1327.

6. J. A. C. S. 1917, **39**, 364; abst. J. S. C. I. 1917, **36**, 454.

7. Mining Sci. Press, 1918, **117**, 415; abst. C. A. 1919, **13**, 11. J. Craig (J. S. C. I. 1919, **38**, 96-T; abst. C. A. 1919, **13**, 1684) oxidizes the SO_2 with H_2O_2 and titrates excess with permanganate.

8. Amer. J. Sci. 1914, **38**, 166; abst. J. S. C. I. 1914, **33**, 917.

9. Chem. Ztg. 1914, **38**, 1057; abst. J. S. C. I. 1915, **34**, 277.

10. Chem. Ztg. 1914, **38**, 601; abst. J. S. C. I. 1914, **33**, 601.

11. Chem. Ztg. 1913, **37**, 465; abst. J. S. C. I. 1913, **32**, 532.

Anderson,¹ the latter having reported obtaining excellent results.

Uses of Sulfur Dioxide.² Apart from its employment as a source of sulfuric acid, other uses of sulfur dioxide are as follows:

- (1) The liquid is used in some types of refrigerating machines.
- (2) The liquid has been proposed as a means of increasing the efficiency of steam engines by allowing the exhaust steam to evaporate sulfur dioxide in an auxiliary cylinder (Behrend and Zimmermann).
- (3) The gas and solution are used in disinfecting and as an antiseptic fumigating, the most convenient source of the gas being the liquid in siphons.³
- (4) In bleaching woolen goods.
- (5) To impart to old barley the yellow color of the new grain
- (6) Liquid sulfur dioxide is employed in the refining of petroleum,⁴ and as a solvent for bituminous substances and resins.
- (7) In tanning to soften dry hides, and in the "pureing" operation.
- (8) For the preparation of sulfites, bisulfites and as a reducing agent.⁵

1. J. Ind. Eng. Chem. 1916, **8**, 258; abst. J. S. C. I. 1916, **35**, 474. For the detection of small amounts of SO₂ see Denigès, Bull. Soc. Pharm. Bordeaux, **54**, 145; abst. J. S. C. I. 1915, **34**, 149. A. Seidell and P. Meserve, J. Ind. Eng. Chem. 1914, **6**, 298. C. di Stefano, Staz. sperim. agrar. ital. 1913, **46**, 780; abst. Chem. Zentr. 1914, **85**, I, 516.

2. C. Lowe and J. Gill, E. P. 4817, 1880; abst. Chem. Ind. 1882, **4**, 65, 140; Wag. Jahr. 1882, **28**, 523. C. Weatherby, E. P. 2115, 1874. J. Garner and H. Clayton, U. S. P. 1173566, 1916; abst. J. S. C. I. 1916, **35**, 469. D. Peniakoff, E. P. 459926, 1912; E. P. 21476, 1912; abst. J. S. C. I. 1913, **32**, 424, 1109; C. A. 1914, **8**, 995, 3224; Chem. Ztg. Rep. 1914, **38**, 128. W. Estor and M. Terrero, E. P. 1457, 1868.

3. T. Clayton, E. P. 18108, 1909; abst. C. A. 1911, **5**, 128; J. S. C. I. 1910, **29**, 588. C. Galaine and H. Hulbert, Compt. rend. 1916, **162**, 363. F. Fischer and W. Glud, Ber. 1916, **49**, 1469; abst. Chem. Zentr. 1916, **87**, II, 1089. J. Moore and F. Martin, U. S. P. 700537, 1902; abst. J. S. C. I. 1902, **21**, 870; J. A. C. S. 1902, **24**, 519.

4. L. Edeleanu, Petroleum, **9**, 862; Bull. Amer. Min. Eng. 1914, 2313; abst. C. A. 1914, **8**, 3626.

5. G. Stebbins, D. R. P. 173976; abst. Wag. Jahr. 1906, **52**, I, 420. E. Basse and G. Faure, D. R. P. 103064; abst. Wag. Jahr. 1899, **45**, 358. R. Dietz and A. Billing, D. R. P. 55652; abst. Wag. Jahr. 1891, **37**, 1148. E. Duviolsart, D. R. P. 210804; abst. Wag. Jahr. 1909, **55**, I, 370. Dittler & Co., D. R. P. 30844; abst. Wag. Jahr. 1885, **31**, 209. Friedrich & Co. and F. Hirsch, D. R. P. 228538; abst. Wag. Jahr. 1910, **56**, I, 432; D. R. P. 247005; abst. Wag. Jahr. 1912, **58**, I, 374. Maschinenbauanstalt Golzern, D. R. P. 77069; abst. Wag. Jahr. 1894, **40**, 1061. A. Höpfner, D. R. P. 138028; abst. Wag. Jahr. 1903, **49**, I, 306. T. Hutchins, L. Hargreaves and A. Dunningham, E. P. 10556, 1915; abst. J. S. C. I. 1916, **35**, 1015. R. Payelle and E. Sidler, D. R. P. 80390; abst. Wag. Jahr. 1895, **41**, 422. E.

Sulfur Trioxide¹ and Contact Sulfuric Acid. The general principles of the contact process of sulfuric acid manufacture

Raynaud, Belg. P. 147589, 1900. H. Specketer and E. Marburg, U. S. P. 1169365, 1916. O. Spinzig and A. Wanning, Norw. P. 22801; abst. Chem. Ztg. 1913, **37**, 244.

1. R. Adie, J. C. S. 1889, **59**, 157; 1891, **59**, 230; Ber. 1891, **24**, 620-R; Chem. News, 1889, **59**, 58; Ber. 1889, **22**, 432-R. G. Aime, J. pharm. 1835, **21**, 87; J. prakt. Chem. 1835, **6**, 79. Aktienges für Zinkindustrie vorm. Grillo u. Schröder, D. R. P. 102244 and 115333. D. R. P. 138695, 1902; abst. Chem. Centr. 1903, **74**, I, 484. H. Armstrong, J. prakt. Chem. 1870, **109**, 244. Bad. Anilin and Sodafabrik, D. R. P. 140353, 113932, 1898; 142895, 1903. D. R. P. 148196, 1904; 133713, 1902. H. Baker, J. C. S. 1894, **65**, 611. L. Barreswil, Compt. rend. 1847, **25**, 30. G. Beilby, Chem. News, 1904, **90**, 180; Chem. Centr. 1904, **75**, II, 1374. E. Berglund, Lunds. Univers. Arskrift. 12, 13; Ber. 1887, **20**, 584. E. Berl, Zts. ang. Chem. 1905, **18**, 252; Chem. Centr. 1905, **76**, I, 1056. Zts. anorg. Chem. 1904, **42**, 453; Chem. Centr. 1905, **76**, I, 328. M. Berthelot, Compt. rend. 1873, **77**, 1880. **90**, 1511; Annuaire pour l'an public par le Bureau des Longitudes, 395; Compt. rend. 1873, **77**, 27; Jahr. Chem. 1877, **30**, 128. Compt. rend. 1877, **84**, 676; 1880, **90**, 1449, 1510; Jahr. Chem. 1877, **30**, 113; 1880, **33**, 117. Compt. rend. 1878, **86**, 20. B. Bizio, Giorn. di Fis. 1825, **8**, 407; Quart. J. of Sc. **21**, 176. L. Bleekrode, Wied. Ann. Phys. 1878, (2), **3**, 161; Jahr. Chem. 1878, **31**, 148. C. Blondeau, Compt. rend. 1849, **29**, 405. F. Bode, Dingl. Poly. 1875, **215**, 322. M. Bodenstein, Zts. Electrochem. 1903, **9**, 696; Jahr. Chem. 1903, **56**, 222. G. Bodländer and K. Köppen, Zts. Electrochem. 1903, **9**, 559, 787; Chem. Centr. 1903, **74**, II, 531, 1028. A. Brüning, Ann. 1856, **98**, 377. H. L. Buff, Ann. Pharm. Suppl. 1866, **4**, 120; Jahr. Chem. 1866, **19**, 18. H. Buff and A. W. Hofmann, Ann. 1860, **113**, 129; Jahr. Chem. 1860, **13**, 30. A. Bussy, Ann. Chim. Phys. 1824, **26**, 411. F. Clausnitzer, Ber. 1878, **11**, 2012. R. D'Arcy, J. C. S. 1889, **56**, 155; Ber. 1889, **22**, 434-R. H. Deacon, E. P. 753, 1682, 1871. M. Dennstedt and C. Ahrens, Zts. anal. Chem. 1896, **35**, 1; Zts. anorg. Chem. 1895, 337; Chem. Centr. 1896, **67**, I, 508. A. D'Heureuse, Pogg. Ann. 1848, **75**, 255; Ann. 1848, **68**, 242; Jahr. Chem. 1847-1848, **1**, 372. H. Deville, Bull. Soc. Chim. 1865, (2), **3**, 366; Jahr. Chem. 1865, **18**, 59. A. Ditte, Compt. rend. 1900, **131**, 143; Chem. Centr. 1900, **71**, II, 423. E. Divers, J. C. S. 1886, **49**, 584; Jahr. Chem. 1886, **39**, 334. E. Drechsel, J. prakt. Chem. 1870, **112**, 20; Jahr. Chem. 1871, **24**, 212. P. Eitner, Ber. 1892, **25**, 462; Jahr. Chem. 1892, **45**, 897. A. Engelhardt, Bull. Acad. St. Petersburg, 1858, **16**, 378; J. prakt. Chem. 1858, **75**, 363. V. Hölbling and H. Dietz, D. R. P. 142144 and 149677; abst. Chem. Centr. 1903, **74**, II, 76; 1904, **75**, I, 769. Evans, Pharm. J. Trans. **8**, 127; Jahr. Chem. 1847-1848, **1**, 370. Farbwerke vorm. Meister, Lucius u. Brüning, D. R. P. 105876; 135887, 1902. D. R. P. 136134, 1902. N. Fischer, Pogg. Ann. 1829, **16**, 119. Fortmann, Dingl. Poly. 1868, **187**, 155. A. Geuther, Ann. 1859, **109**, 129; Jahr. Chem. 1859, **12**, 82. Ann. 1859, **111**, 177; Jahr. Chem. 1859, 83. O. Gruber, D. R. P. 27726, 1884. J. S. C. I. 1885, **4**, 116. F. Gumpert, J. prakt. Chem. 1884, **138**, 87; Jahr. Chem. 1884, **37**, 486. G. Gustavson, Ber. 1873, **6**, 9; Jahr. Chem. 1873, **26**, 209. E. de Haën, D. R. P. 128616; abst. Wag. Jahr. 1902, **48**, I, 290. M. Hännisch and E. Schröder, D. R. P. 42215. W. Hempel, Ber. 1890, **22**, 1455. G. Hess, Pogg. Ann. Phys. 1842, **56**, 471. R. Hill, Chem. News, 1895, **72**, 75; Jahr. Chem. 1895, **48**, 527. W. Hodgkinson and F. Lowndes, Chem. News, 1888, **57**, 193; Ber. 1888, **21**, 513. A. Hofmann and G. Buckton, Ann. Pharm. 1856, **100**, 129; J. C. S. 1857, **9**, 241; Jahr. Chem. 1856, **9**, 508. J. Jullion, E. P. 11425, 1846. H. Kämmerer, J. prakt. Chem. 1861, **83**, 72. G. Kerpeler, Zts. ang. Chem. 1902, **15**, 809; Chem. Centr. 1902, **73**, II, 727. R. Knetsch, Ber. 1901, **34**, 4069. Chem. Centr. 1902, **73**, I, 282. F. Krafft,

have already been briefly described (p. 1009). The chief feature of the method which has made great progress in recent years, is

Ber. 1890, **23**, 2389; Jahr. Chem. 1890, **43**, 1771. F. Küster, Zts. anorg. Chem. 1904, **42**, 453; Chem. Centr. 1905, **76**, I, 328. A. Lotka, Chem. Eng. 1909, **9**, 91; abst. C. A. 1909, **3**, 1671. G. Lunge, D. R. P. 3166, 1888. G. Lunge and G. Pollitt, Zts. ang. Chem. 1902, **15**, 1105; Chem. Centr. 1902, **73**, II, 1480. G. Lunge and K. Reinhardt, Zts. ang. Chem. 1904, **17**, 1041; Chem. Centr. 1904, **75**, II, 861. G. Lunge and F. Salathe, Ber. 1877, **10**, 1824; Chem. Ztg. 1883, **7**, 29. G. Magnus, Pogg. Ann. 1832, **24**, 610; 1858, **104**, 553. F. Mahla, Ann. 1852, **81**, 255; Jahr. Chem. 1852, **5**, 339. C. de Marignac, Arch. sc. phys. nat. 1853, **22**, 225; 1877, **58**, 2289; Ann. Chim. Phys. 1853, (3), **39**, 184; Ann. 1853, **86**, 228; Jahr. Chem. 1853, **6**, 324; 1877, **30**, 209. V. Merz, J. prakt. Chem. 1866, **99**, 181. R. Messel, E. P. 186, 1828, 1878; abst. Chem. Tech. Rep. 1878, **17**, I, 361. F. Meyer, J. S. C. I. 1903, **22**, 348; Chem. Centr. 1903, **74**, I, 1446. A. Michaelis, Zts. Chem. 1871, **14**, 151. F. Muck, Ber. 1875, **8**, 1283. R. Nasini, Ber. 1882, **15**, 2885. A. Nobel and G. Fehrenbach, D. R. P. 30803; Ber. 1885, **18**, 201-R. G. Oddo, Gazz. chim. ital. 1901, **31**, II, 158; Chem. Centr. 1901, **72**, II, 969. W. Odling, J. C. S. 1855, **7**, I, G. Osann, Dingl. Poly. 1859, **151**, 158. E. Perman, Proc. Roy. Soc. 1890, **48**, 57; Jahr. Chem. 1890, **43**, 111. P. Phillips, E. P. 6096, 1831. A. Pinner and F. Klein, Ber. 1878, **11**, 1825; Jahr. Chem. 1878, **31**, 328. R. Piria, Cimento. **2**, 293; Jahr. Chem. 1855, **8**, 308. V. Ragsine and P. Dworkowitsch, D. R. P. 43453, 1888. W. Rath, D. R. P. 22118, Dingl. Poly. 1883, **249**, 453; Jahr. Chem. 1883, **36**, 1685. H. Rebs, Ann. 1888, **246**, 356; Ber. 1888, **21**, 596-R. F. Reich, J. prakt. Chem. 1863, **90**, 176. C. Reese, J. S. C. I. 1903, **22**, 351; Chem. Centr. 1903, **56**, I, 1446. H. Rose, Pogg. Ann. 1834, **24**, 140. E. Russell and N. Smith, Proc. Chem. Soc. 1900, **16**, 41; J. C. S. 1900, **77**, 340. A. Scheurer-Kestner, Compt. rend. 1875, **80**, 1230; Jahr. Chem. 1875, **28**, 162; Ber. 1877, **10**, 1824; Compt. rend. 1884, **99**, 917; Jahr. Chem. 1884, **37**, 342; 1885, **38**, 2059. H. Schlundt, J. Phys. Chem. 1901, **5**, 503; abst. J. C. S. 1902, **82**, ii, 2. A. Schmersahl and J. Bouck, E. P. 183, 1855. R. Schenck, Ann. 1901, **316**, 1; Chem. Centr. 1901, **72**, I, 1305. H. Schröder, Wied. Ann. Phys. 1882, **16**, 660; Jahr. Chem. 1882, **35**, 31. R. Schuberth, D. R. P. 52000; Ber. 1890, **23**, 515. C. Schultz-Sellack, Pogg. Ann. 1870, **139**, 480; Ber. 1870, **3**, 215. Ber. 1871, **4**, 15, 109, 110. H. Schulze, Ber. 1884, **17**, 2705. A. Stavenhagen, Zts. ang. Chem. 1893, **6**, 283; Jahr. Chem. 1893, **46**, 373. G. Stone, J. S. C. I. 1903, **22**, 350; Chem. Centr. 1903, **74**, I, 1446. M. Teplow, J. Russ. Phys. Chem. Soc. 1888, Suppl. 1-12; Ber. 1889, **22**, 1-R. J. Thomsen, Ber. 1870, **3**, 500; 1873, **6**, 713. Pogg. Ann. 1873, **150**, 32. W. Thornthwaite, E. P. 188, 1854. A. Truemann, E. P. 982, 1854. Verein Chem. Fabriken in Mannheim, D. R. P. 107995, 1898; 108446, 1898. D. R. P. 154084. Verein Chem. Fabriken and A. Clemm, D. R. P. 142410. H. Vernon, Chem. News, 1891, **64**, 54; Jahr. Chem. 1891, **44**, 180. F. C. Vogel, Schweigg. J. 1812, **4**, 121, 123. G. Wach, Schweigg. J. 1827, **50**, 1. P. Walden, Zts. anorg. Chem. 1900, **25**, 209; abst. Jahr. Chem. 1900, **53**, 87. J. Walz, Chem. News, 1871, **23**, 245; Amer. Chemist, 1871, (2), **1**, 242; Bull. Soc. Chem. 1871, (2), **16**, 75; Jahr. Chem. 1871, **24**, 215. R. Weber, Pogg. Ann. 1864, **123**, 233, 337; 1871, **142**, 602; Ber. 1887, **20**, 86, 87. Pogg. Ann. 1876, **159**, 313; Jahr. Chem. 1876, **29**, 174; Ber. 1886, **19**, 3, 86, 3187. Verh. Ges. Naturforocher, 1891, 72; Chem. Centr. 1892, **63**, II, 105. J. prakt. Chem. 1882, (2), **25**, 218, 224; Jahr. Chem. 1882, **35**, 228, 229. M. Wilde, Ber. 1874, **7**, 356. C. Winkler, Dingl. Poly. 1875, **218**, 128; 1879, **233**, 142; Jahr. Chem. 1875, **28**, 161; D. R. P. 4566, 1878. J. Wolters, D. R. P. 3110, 1878; 6091, 1878; Chem. Ind. 1878, **1**, 329; Dingl. Poly. 1878, **230**, 451; Ber. 1878, **11**, 1946; Jahr. Chem. 1878, **31**, 1122; Ber. 1881, **14**, 122.

the use of a catalyst to promote the union of sulfur dioxide and oxygen, the latter usually in the form of air, to form sulfur trioxide: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$. The reaction is a reversible one, a part only of the sulfur dioxide being converted into trioxide, the proportion depending mainly upon the temperature. An equilibrium is established, and the proportion of sulfur dioxide converted into trioxide is greater the lower the temperature. With the use of an excess of sulfur dioxide or of oxygen,¹ the conversion increases in accordance with the law of mass-action. In practice the object is to convert as large a proportion as possible of the sulfur dioxide into trioxide, and therefore an excess of oxygen (air) is used. The sulfur trioxide is then brought in contact with sulfuric acid, either concentrated when fuming sulfuric acid or oleum is produced, or acid containing water, when the strength of the acid is increased and strong sulfuric acid is formed. The gases containing sulfur trioxide are not brought in contact with water as such, because in that case a dense fume of droplets of sulfuric acid results, difficult to condense and utilize.

The history of the Contact Process may be said to have begun with the discovery of the catalytic action of platinum by Humphrey Davy in 1818. He used platinum wire, and showed that it could promote many chemical reactions, such as the union of oxygen with hydrogen, carbon monoxide, hydrocarbons, or cyanogen.² J. Doebereiner in 1832³ found that finely divided platinum, in the form of sponge, obtained by the ignition of ammonium platinichloride, is much more active than the massive metal, and numerous investigations have since been made on the catalytic activity of platinum and other contact masses.⁴ The action

1. J. Partington, "The Alkali Industry," London, 1918, 41.

2. H. Davy, Phil. Trans. 1817, **107**, 45, 77. An account of the history of the contact process is given by F. Winteler, Zts. ang. Chem. 1905, **18**, 1512, 1654. For the general theory of catalysis, see J. Mellor, "Chemical Statics and Dynamics," London, 1904.

3. Schw. J. **34**, 91; **38**, 321. Gilb. Ann. 1823, **74**, 269. Schw. J. **39**, 159; **42**, 60; **63**, 465. "Ueber neu entdeckte und höchst merkwürdige Eigenschaften des Platins," Jena, 1823.

4. Ferric oxide (Verein Chem. Fabriken in Mannheim, D. R. P. 107995, 108446, 1898). Ferric arsenate, and iron-free arsenic pentoxide. Silica exerts appreciable action at 700°, the yield being 10%. Jena glass and Berlin porcelain have a very slight action (G. Lunge and K. Reinhardt, Zts. ang. Chem. 1904, **17**, 1041; abst. Chem. Centr. 1904, **75**, II, 861). Addition of arsenic to ferric oxide increases the catalytic action (Ver. Chem. Fabr. in Mannheim, D. R. P. 154084); however, at first decreasing the yield (F. Küster, Zts. anorg. Chem. 1904, **42**, 453; abst. Chem. Centr. 1905, **76**, I, 328).

of these materials, which undergo no permanent chemical change in the course of the chemical reactions they induce, is incompletely understood, even at present. Two theories have been proposed to account for their activity. According to M. Faraday,¹ the contact substance possesses the capacity of condensing on its surface the gases which it causes to interact, and the latter, being then in a condition similar to that in a strongly compressed mixture of the gases, are brought into a condition favorable for reaction. According to A. de la Rive,² on the other hand, one or more of the gases first of all forms unstable compounds with the catalytic material, which then react with the other gas, or gases, leaving the catalyst unchanged and capable of again reacting. Thus, in the oxidation of hydrogen in the presence of spongy platinum, it is assumed that an oxide of platinum, possibly PtO, is first formed, and then is reduced by the hydrogen: $\text{PtO} + \text{H}_2 = \text{Pt} + \text{H}_2\text{O}$. It appears from the recorded investigations³ that both influences may play a part in the different kinds of reactions. The sum total of evidence appears to favor the intermediate compound theory in the case under discussion.

The utilization of the contact action of platinum in the production of sulfuric acid was first made by Peregrine Phillips, of Cupric oxide and chromic oxide (Ver. Chem. Fabr. in Mannheim, D. R. P. 142410). Ferric oxide, cupric oxide, chromic oxide, coated with platinum (Bad. Anilin u. Sodafabrik, D. R. P. 140353). Platinized lumps of water soluble salts such as magnesium sulfate (D. R. P. 138695). Sulfates of the rare earths (V. Höbling and H. Ditz, D. R. P. 142144, 149677, 1904). Vanadium compounds, especially vanadium pentoxide (E. de Haën, D. R. P. 128616; F. Küster, Zts. anorg. Chem. 1904, **42**, 453; abst. Chem. Centr. 1905, **76**, I, 328). For the properties which characterize a contact substance, see G. Keppeler, Zts. ang. Chem. 1902, **15**, 809; abst. Chem. Centr. 1902, **73**, II, 727. For re-activating of poisoned platinum contact masses, see A. G. Zinkindustrie vorm. Grillo & Schröder, D. R. P. 102244, 115333. Farbwerke vorm. Meister, Lucius & Brüning, D. R. P. 135887, 1902. Badische Anilin u. Sodafabrik, D. R. P. 142895, 148196. For further information on the production of sulfur trioxide by the contact process, see H. Angerstein, D. R. P. 26959, 1883. Farbwerke Meister, Lucius and Brüning, D. R. P. 105876, 1899; 109483, 1900. Verein Chem. Fabriken in Mannheim, D. R. P. 136134, 1902. Bad. Anilin u. Sodafabrik, D. R. P. 133713, 1902. G. Lunge and G. Pollitt, Zts. ang. Chem. 1902, **15**, 1105; abst. Chem. Centr. 1902, **73**, II, 1480. F. Meyer, J. S. C. I. 1903, **22**, 348; abst. Chem. Centr. 1903, **74**, I, 1446. G. Stone, J. S. C. I. 1903, **22**, 350; abst. Chem. Centr. 1903, **74**, I, 1446. C. Reese, J. S. C. I. 1903, **22**, 351; abst. Chem. Centr. 1903, **74**, I, 1446.

1. Phil. Trans. 1834, **124**, 1.

2. Pogg. Ann. 1839, **46**, 489, 492; 1841, **54**, 386, 397. A. de la Rive and F. Marcet, Ann. Chim Phys. 1828, **39**, 328.

3. W. Bancroft, Trans. Amer. Electrochem. Soc. 1917, **32**, 439, 457; abst. J. S. C. I. 1917, **36**, 1169.

Bristol, England, in 1831.⁶ He took out a patent for his discovery, but nothing practical ever came of it. He found that the platinum rapidly became inactive, or "poisoned," and the process then stopped.¹

The contact process became practical when C. Winkler² proposed the use of a mixture of sulfur dioxide and oxygen, obtained by dropping strong sulfuric acid on red-hot bricks: $\text{H}_2\text{SO}_4 = \text{SO}_2 + \text{O} + \text{H}_2\text{O}$. The gas was dried and passed over the platinumized asbestos. This was not a method of making sulfuric acid, but of fuming sulfuric or sulfur trioxide. In the same year (1875), S. Squire and R. Messel in England³ carried out this process, and later on S. Squire used sulfur dioxide from the combustion of sulfur, purified by dissolving in water under 4 atm. pressure and then expelling with steam. This process was used by the Thann Chemical Co., in Alsace, in 1881. Other plants were erected in Germany and elsewhere, and numerous patents were taken out from 1875 to 1898, mostly, however, based on the process devised

1. P. Phillips, E. P. 6096, 1831. For the development of the contact process, see G. Magnus, Pogg. Ann. 1832, **24**, 610. J. Doberciner, Pogg. Ann. 1832, **24**, 609. A. Hofmann, Report of the Jury on the Exhibition of 1862, 9. J. Schneider, Dingl. Poly. 1847, **106**, 395; see also Compt. rend. 1847, **25**, 931; Mon. Univers. 1848, No. 1217; Bull. Soc. d'Encouragement, 1848; abst. Dingl. Poly. 1848, **107**, 159, 362; **109**, 354. W. Petrie, E. P. 590, 1852. W. Thornthwaite, E. P. 188, 1851. R. Piria, Cimento, **2**, 293; abst. Jahr. Chem. 1855, **8**, 308. All of the preceding used platinum, or platinumized asbestos. R. Laming, E. P. 12261, 1848, used pumice-stone prepared by boiling in sulfuric acid, immersing in water containing a little ammonia, drying and heating in a retort to 316° C. with about 1% of manganese peroxide, allowing it to cool out of contact with the air. L. Blondeau (Compt. rend. 1849, **29**, 405) employed argillaceous sand, at red heat in a porcelain tube, to cause sulfur dioxide, air and steam to react with the formation of sulfuric acid. F. Wöhler (Ann. 1852, **81**, 255) found that oxides of copper, iron or chromium, or mixtures of these, would act as catalyzers at a low red heat. See Wag. Jahr. 1859, **5**, 144. G. Robb (E. P. 731, 788, 1853) used ferric oxide resulting from the burning of pyrites, manganese dioxide, etc. A. Trueman (E. P. 982, 1854) employed platinum wire, or pumice stone impregnated with platinum salts and ignited, and iron, copper, chromium and manganese oxides, at a red heat. W. Thornthwaite, E. P. 188, 1854. A. Schmersahl and J. Bouck (E. P. 183, 1855) used asbestos, a mixture of copper and chromium oxides, platinum, in sheets or wire, pumice, coke or charcoal. Silica is mentioned by W. Petrie (E. P. 590, 1852; 2095, 1856), but it does not appear that it was used as a contact substance. W. Hunt, E. P. 1919, 1853, used red hot pebbles. Plattner, "Die metallurgischen Röstprozesse, Freiberg, 1856, 334. H. Deacon (E. P. 753, 1682, 1871) tried copper sulfate, but without practical success.

2. Dingl. Poly. 1875, **218**, 128; abst. J. C. S. 1876, **29**, 783; Bull. Soc. Chim. 1876, **25**, 43; Chem. Tech. Rep. 1875, **14**, I, 221; Jahr. Chem. 1875, **28**, 161.

3. J. S. C. I. 1885, **4**, 520.

by Squire and Messel. In every case the advice of C. Winkler was followed, and a mixture of gases in the exact ratio $\text{SO}_2:\text{O}$ was used, although the law of mass action clearly indicated the advantage of an excess of oxygen.

The first impetus to large scale production resulted from the publication in 1898¹ of a paper by R. Knietsch, of the Badische Company, in which the important proposition was stated that it was possible so to purify the gases from pyrites kilns that they could be used in the contact process without causing poisoning of the platinum. He found that when the dust, sulfuric acid mist, and arsenic in these gases are first removed, the contact mass remains active for long periods. Simultaneously a similar discovery was made by Krauss and von Berneck, of Meister, Lucius & Brünig, of Höchst, who took out patents at the same time with the Badische firm. Many seemingly unimportant modifications of the process have been the subject of more recent patents, but a real advance has been the method of M. Schroeder and W. Grillo,² in which the contact mass is comprized of magnesium sulfate as an inert carrier, impregnated with a platinum salt and heated so as to swell up and expose a large surface, which becomes covered with finely divided platinum formed by the decomposition of the salt.

The equilibrium $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ is maintained at 450° with 91% of SO_3 ; if air is used instead of oxygen so that the proportions of SO_2 and O_2 are unchanged, the yield is 91%. The best result is obtained when the oxygen is present in three times the theoretical amount, viz.: $2\text{SO}_2 + 3\text{O}_2$, which happens to be the ratio given by ordinary pyrite burners. With these gases, and a temperature of 400° – 450° , a conversion of 98% is commercially attainable. Heat is evolved in the reaction, and the catalytic mass must be kept cool by allowing a portion of the cold gases to sweep over the outside of the containing vessel. With an initial gas containing 7.0% SO_2 by volume, 10.4% O_2 , and

1. Ber. 1901, **34**, 4069; abst. J. C. S. 1902, **108**, ii, 132; J. S. C. I. 1902, **21**, 172, 343; Bull. Soc. Chim. 1902, **28**, 305; Mon. Sci. 1902, **58**, 289; Rep. Chim. 1902, **2**, 162; Rev. Chim. 1902, **5**, 49, 83; Chem. Centr. 1902, **73**, 1, 282; Chem. Zts. 1901–1902, **1**, 273, 305, 474, 479, 580, 660, 709; Jahr. Chem. 1901, **54**, 242; Meyer Jahr. Chem. 1901, **11**, 320; Wag. Jahr. 1901, **47**, 1, 418; Zts. ang. Chem. 1903, **16**, 567, 623.

2. D. K. P. 102244, 1898; abst. Wag. Jahr. 1899, **45**, 366; Chem. Centr. 1899, **70**, I, 1176; Chem. Ztg. 1899, **23**, 426; Zts. ang. Chem. 1899, **12**, 229; Jahr. Chem. 1899, **52**, 424; Mon. Sci. 1899, **54**, 145.

82.6% N_2 , the maximum equilibrium yields at different temperatures are as stated:¹

| Temperature C. | Equilibrium Conversion of SO_2 to SO_3 . Per cent. |
|----------------|---|
| 434° | 97 |
| 550° | 85 |
| 645° | 60 |

From this it appears to be advantageous to work at as low a temperature as possible. It is impracticable, however, to go below 450°, as the speed of reaction then becomes very slow.² In practice 400°–450° is aimed at. This is evident from the curves given by Knietsch,³ in which the first set represent the percentage of SO_3 formed in the various mixtures at varying temperatures, each curve corresponding with a different flow rate. By increasing the latter, the temperature for optimum conversion increases but the yield decreases. In the second set of curves the influence of time of contact with the catalyst is shown, the best temperature being 450°.

As already stated, the comparative costs of the contact and chamber processes run very close when ordinary acid is to be made, but the contact process is the cheaper, at least under European conditions, when a very strong acid is to be manufactured.

Many contact substances other than platinum have been proposed, but with the exception of ferric oxide⁴ these do not appear to have been used to any considerable extent. An account of the various catalysts appears on pages 1113 to 1121 for sulfuric manufacture, and on pages 915 to 918 for synthetic nitric acid formation.

Apparatus Used in the Contact Process. The apparatus used in carrying out the contact process must comprise arrangements whereby the sulfur dioxide and air are brought into intimate association with the contact mass for a sufficient length of time

1. F. Haber, "Thermodynamics of Technical Gas Reactions," transl. Lamb, 1908, p. 199. This book contains a valuable account of the theory of the contact process.

2. M. Bodenstein and C. Fink, *Zts. physik. Chem.* 1907, **60**, 1, 46; *abst. Jahr. Chem.* 1905–1908, I, 990.

3. See J. Partington, "Alkali Industry," Figs. 14 and 15.

4. L. and P. Wöhler and W. Plüdermann, *Zts. physik. Chem.* 1908, **62**, 641; *abst. J. S. C. I.* 1908, **27**, 684. F. Wöhler, *Ann.* 1852, **81**, 255. G. Lunge and G. Pollitt, *Zts. ang. Chem.* 1902, **15**, 1105.

for the conversion, or to bring about equilibrium at the temperature of working, and devices whereby the temperature of the catalyst, on the surface of which the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ occurs, is maintained at a suitable degree by means of preheating or heat-interchanging devices. A great number of arrangements have been proposed for the purpose of fulfilling these conditions, but comparatively few are at present in actual use. The systems which have been extensively used are:

- (1) The Badische Process.
- (2) The Process of the Farbwerke Meister, Lucius and Brüning, of Höchst.
- (3) The Schroeder-Grillo Process.
- (4) The Mannheim Process.
- (5) The Tentelew Process.

Of these, all except No. 4 use platinum in various forms as the catalytic material. In addition, many other forms of apparatus have been described,¹ but detailed description of these is hardly

1. A. G. für Zinkindustrie, Aust. P. 12287, 1903. H. Blackmore, U. S. P. 828268, 1906; 778099, 1904; abst. Chem. Zts. 1905, **4**, 270; 1906, **5**, 496; Mon. Sci. 1905, **63**, 116; 1907, **67**, 53; J. A. C. S. 1905, **27-R**, 502. H. Briegleb, E. P. 11792, 1901; abst. J. S. C. I. 1902 **21**, 706. C. Brockbank, U. S. P. 1157293; abst. C. A. 1915, **9**, 3335. C. Daub and J. Deuther, E. P. 9536, 1902. F. P. 322834, 1902. U. S. P. 731758; abst. J. S. C. I. 1902, **21**, 1138; 1903, **22**, 364; Chem. Zts. 1903, **2**, 158, 716; 1904, **3**, 13; Mon. Sci. 1903, **59**, 127, 172; J. A. C. S. 1904, **26-R**, 39. G. Eschellmann, E. P. 23419, 1909; abst. C. A. 1911, **5**, 163; J. S. C. I. 1910, **29**, 422. G. Eschellmann and A. Harmuth, U. S. P. 937148; abst. C. A. 1910, **4**, 371. U. S. P. 792205, 1905. 1036473; abst. C. A. 1912, **6**, 3315; Chem. Ztg. Rep. 1913, **37**, 32; J. A. C. S. 1906, **28-R**, 75. General Chemical Co. (J. Herreshoff, assignor), U. S. P. 719332; 722981; abst. J. S. C. I. 1903, **22**, 212, 494; Chem. Zts. 1903, **2**, 529; 1904, **3**, 13; J. A. C. S. 1903, **25-R**, 378, 491 (W. Ferguson, assignor), U. S. P. 723595, 723596. E. P. 6824, 1903. F. P. 330521, 1903; abst. J. S. C. I. 1903, **22**, 495, 742, 1086; Mon. Sci. 1903, **59**, 170; 1904, **61**, 67; Chem. Zts. 1904, **3**, 13; J. A. C. S. 1903, **25-R**, 494; Chem. Ztg. 1903, **27**, 372. (P. Herreshoff, assignor) U. S. P. 737626, 1903; abst. J. S. C. I. 1903, **22**, 1086; Chem. Zts. 1904, **3**, 291; J. A. C. S. 1904, **26-R**, 190; Mon. Sci. 1903, **59**, 183. (G. Eschellmann and A. Harmuth, assignors) U. S. P. 937147; abst. C. A. 1910, **4**, 370. U. S. P. 1030508; E. P. 23419, 1909; abst. J. S. C. I. 1910, **29**, 422; 1912, **31**, 687. U. S. P. 1036473; abst. C. A. 1912, **6**, 3315. The Grasselli Chemical Co. (I. Lihme, assignor), U. S. P. 1103522, 1914; abst. C. A. 1914, **8**, 3102; Zts. ang. Chem. 1916, **29**, 1, 116; Chem. Ztg. Rep. 1915, **39**, 114; Mon. Sci. 1914, **81**, 178. W. Grosvenor, U. S. P. 1036609, 1036610; abst. C. A. 1912, **6**, 3315; Chem. Ztg. Rep. 1913, **37**, 32. E. Hänisch and M. Schroeder, U. S. P. 384841, 1888. E. P. 9188, 1887; abst. J. S. C. I. 1887, **6**, 599; Chem. Centr. 1887, **58**, 1419. J. Herreshoff, U. S. P. 719332, 719333, 1903; abst. J. S. C. I. 1903, **22**, 212. H. Hilbert and Bayerische Akt. Ges. f. Chem. u. Landw. Fabrikate, Aust. P. 26211, 1901; cf. Aust. P. 484. E. P. 9453, 1903. F. P. 331289, 1903. Swiss P. 28076, 1903; abst. J. S. C. I. 1903, **22**, 1035; Chem. Zts. 1906, **5**, 571; Mon. Sci. 1904, **61**, 68.

necessary here, as they introduce but very few novel features. Many refer to minor improvements in the construction or method of working of known processes. The above five named, however, will be described in detail in the sequel.

Processes in the Contact Methods. Although the various contact methods differ in detail, there are many underlying principles common to nearly all which may be considered in a general manner before proceeding to the special descriptions. These comprize:

(1) The preliminary purification of the burner gases.

V. Hoebbling and H. Ditz, Aust. P. 15377, 1903; abst. Chem. Zts. 1904, **3**, 433. D. R. P. 142144; abst. Zts. ang. Chem. 1903, **16**, 583; Chem. Centr. 1903, **74**, II, 76; Jahr. Chem. 1903, **56**, 345; Chem. Ztg. 1903, **27**, 509; Wag. Jahr. 1903, **49**, I, 260; Mon. Sci. 1904, **61**, 6; 1905, **63**, 135; Chem. Zts. 1904, **3**, 13, 276, 504. Belg. P. 166523, 1902. H. Howard, U. S. P. 1028880, 1912; abst. J. S. C. I. 1912, **31**, 686; C. A. 1912, **6**, 2199; Chem. Ztg. Rep. 1912, **36**, 405. W. Kauffmann, E. P. 7074, 1904; abst. J. S. C. I. 1905, **24**, 90. C. Krauss and J. Wach (assignors to Farbwerke Meister, Lucius & Brüning), U. S. P. 677670, 1901; abst. Mon. Sci. 1901, **57**, 281. M. Leblanc and C. Krauss (assignors to Farbwerke Meister, Lucius & Brüning), U. S. P. 726076, 1903; abst. Mon. Sci. 1903, **59**, 170; Chem. Zts. 1903, **2**, 614; 1904, **3**, 12; J. A. C. S. 1903, **25-R**, 525. J. McFetridge, U. S. P. 988646, 1911; abst. Mon. Sci. 1912, **77**, 19. P. Naef, E. P. 18191, 1900; 11976, 14977, 1901; abst. J. S. C. I. 1902, **21**, 1027, 1076. M. Neumann, D. R. P. 187077; abst. C. A. 1908, **2**, 576; J. S. C. I. 1908, **27**, 502; Zts. ang. Chem. 1907, **20**, 795; Chem. Zentr. 1907, **78**, II, 1280; Jahr. Chem. 1905-1908, I, 1624; Chem. Zts. 1908, **7**, 556; Chem. Ztg. Rep. 1907, **31**, 392; Wag. Jahr. 1907, **53**, I, 340. B. Parodi-Delfino, E. P. 113017, 1917; abst. C. A. 1918, **12**, 1237; J. S. C. I. 1918, **37**, 149-A. R. Pictet, E. P. 480294; abst. J. S. C. I. 1917, **36**, 137; Ann. Rep. Chem. Soc. Ind. 1917, **2**, 191. J. Porter, E. P. 22080, 1914; abst. J. S. C. I. 1915, **34**, 1197. E. Raynaud and L. Pierron, U. S. P. 736876, 751941; E. P. 16254, 1900; abst. J. S. C. I. 1901, **20**, 42; 1903, **22**, 1045; Chem. Ztg. 1902, **26**, 54; Mon. Sci. 1902, **58**, 154, 1903, **59**, 182; Chem. Zts. 1904, **3**, 82, 492; J. A. C. S. 1904, **25-R**, 141, 404. A. Schillot, U. S. P. 700249, 1902; E. P. 2192, 1909; abst. C. A. 1910, **4**, 847; J. S. C. I. 1909, **28**, 1497; 1902, **21**, 839; Chem. Zts. 1903, **2**, 275; J. A. C. S. 1902, **24**, Mon. Sci. 1902, **58**, 184. See also E. P. 21616, 1898; abst. J. S. C. I. 1899, **18**, 144. Belg. P. 152550, 1900; 164819, 1902. G. Stone, U. S. P. 695180, 1902; abst. J. S. C. I. 1902, **21**, 476; Chem. Zts. 1903, **2**, 9; J. A. C. S. 1902, **24**, 431; Mon. Sci. 1902, **58**, 184 (assignor to N. J. Zinc Co.); U. S. P. 711186, 1902; abst. J. S. C. I. 1902, **21**, 1395; Chem. Zts. 1903, **2**, 158, 274; J. A. C. S. 1903, **25-R**, 242. Tentelaw Chemical Co. (G. Eschellmann and A. Har-muth, assignors), U. S. P. 792205. E. P. 11969, 1902; abst. J. S. C. I. 1903, **22**, 695; Mon. Sci. 1905, **63**, 140; J. A. C. S. 1906, **28-R**, 75. Verein Chemischer Fabriken in Mannheim, D. R. P. 142855. Aust. P. 15339, 1903. F. P. 323491; 1902; abst. J. S. C. I. 1903, **22**, 495; Chem. Centr. 1903, **74**, II, 535; Jahr. Chem. 1903, **56**, 345; Chem. Ztg. 1903, **27**, 836; Wag. Jahr. 1903, **49**, I, 256; Chem. Zts. 1903, **2**, 314; 1904, **3**, 13, 433. E. Wenmaekers, E. P. 19902, 1901; abst. J. S. C. I. 1902, **21**, 1394; Chem. Ztg. 1903, **27**, 124. E. Wilke, U. S. P. 1270997, 1918; abst. J. S. C. I. 1918, **37**, 579-A; C. A. 1918, **12**, 1913; Ann. Rep. Soc. Chem. Ind. 1918, **3**, 165. G. Wischin, E. P. 12419, 1903; abst. J. S. C. I. 1904, **23**, 714. T. Wolff, U. S. P. 1099530; 1914; abst. C. A. 1914, **8**, 2783.

(2) The efficient mixing of the various gases at all stages.

(3) The absorption of the sulfur trioxide formed.

As regards the initial purification of the gases, this may be said to be the chief factor on which the success or failure of a plant depends. Except in the case of the iron oxide catalyst, when unpurified burner gases are used directly, it is first of all necessary to submit the burner gas to an exhaustive purification before passing it to the contact mass, as otherwise the latter rapidly becomes poisoned and inactive. Even with the iron oxide catalyst, it is imperative that the air used in the pyrite burners should be dried before use.¹

The earlier proposals² refer to the passage of the gases through settling chambers, but this is quite inadequate. G. Gin³ cools the gases, removes SO₃ fog by absorption in sulfuric acid, and then absorbs the SO₂ in water, from which it is driven off by heating. H. Rabe⁴ refrigerates the gas, and filters it through a heavy layer of asbestos. It is then conducted over shelves containing bisulfites to remove SO₃, and then through a tower fed with strong sulfuric acid. G. Stone⁵ draws the mixture through compartments, alternately filters and condenses. The arsenic is also stated to be deposited on wire gauzes or suitable filtering devices. Filtration is also proposed by J. Shields.⁶ M. Scharff and F. Slama⁷ pass the gases over heated oxides of iron, copper, chromium, manganese, or mixtures of these to remove arsenic, and through infusible granular bodies consisting of clay, coke, furnace slag, phosphates and silicates of the alkalis heated to 350°–400°, to effect purification.

In the Badische Process⁸ the gases are treated with steam,

1. W. Hasenbach, U. S. P. 670559, 1901; abst. Mon. Sci. 1901, **57**, 154, 281.

2. A. Bigelow and S. Baldwin, U. S. P. 90067, 1869. R. Laming, Poly. Centr. 1849, **15**, 1310. Dingl. Poly. 1849, **112**, 281; **113**, 228. J. Goodfellow and F. Sabbaton, U. S. P. 140034, 1873.

3. U. S. P. 734849, 1903; abst. Chem. Zts. 1904, **3**, 47, 164; J. A. C. S. 1904, **26-R**, 86; Chem. Ztg. 1903, **27**, 814.

4. U. S. P. 739108, 1903; abst. J. A. C. S. 1904, **26-R**, 195; Mon. Sci. 1904, **61**, 8.

5. U. S. P. 758222, 1904; abst. J. A. C. S. 1904, **26-R**, 471. U. S. P. 711187, 711188, 1902; abst. Chem. Zts. 1903, **2**, 158, 274; Chem. Ztg. 1902, **26**, 1061.

6. U. S. P. 793745, 1905.

7. U. S. P. 798216, 798302, 1905; abst. J. A. C. S. 1906, **28-R**, 177, 178; Mon. Sci. 1906, **65**, 18.

8. R. Knietzsch, U. S. P. 822373, 1906; abst. J. A. C. S. 1906, **28-R**, 539.

then cooled and washed, and finally dried by passing over coke impregnated with sulfuric acid.

O. Jonas¹ removes arsenic from the gases by passage through towers fed with acetylene tetrachloride, or dichlorobenzene. G. Eschellmann² passes the gas through a cooler, then through two coke filters, and finally through a tower fed with milk of lime. J. Herreshoff³ passes the gases through a dust chamber, then through a series of combined scrubbers and coolers, and finally into a drier. H. Hegeler and N. Heinz⁴ mix the gases with cool gases of the same SO₂ content, aspirating them through a tower fed with sulfuric acid, and finally drying. W. Rockliff and J. Booth⁵ submit the gases to the centrifugal action of a spiral deflector, which throws out dust and solid impurities. To remove chlorine, hydrochloric acid, hydrogen sulfide and sulfuric acid mist, C. Reise⁶ cools the gases and passes them over quicklime. The method of electrostatic precipitation has been proposed by F. Cottrell⁷ for the separation of dust and impurities from the gases. The latter are led through a flue containing a number of screens arranged in pairs. The first screen of each pair is fed with dilute sulfuric acid, and the second with fuming sulfuric acid. An acid mist is thus formed, which is precipitated by the electrostatic method. To obviate excessive use of sulfuric acid in drying the gases, H. Howard⁸ first partially dries by cooling. The latter process has also been proposed by J. Herreshoff,⁹ who introduces first a preliminary wash with sulfuric acid of 40° Bé., and then cools from 200° to 100° F.

The gases, after proper purification, are next passed over the contact mass, which, as previously described, consists in the apparatus actually in use almost exclusively of platinum in some

1. U. S. P. 891703, 891775, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 389, Mon. Sci. 1909, **71**, 113.

2. H. Eschellmann, U. S. P. 900500, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 584. H. Eschellmann and A. Harmuth, U. S. P. 937147, 937148; abst. Mon. Sci. 1910, **73**, 82.

3. U. S. P. 940596, 1909.

4. U. S. P. 931868, 1909; abst. Chem. Ztg. Rep. 1909, **33**, 531.

5. U. S. P. 922516, 1909.

6. U. S. P. 989801, 1911; abst. C. A. 1911, **5**, 2159; Chem. Ztg. Rep. 1911, **35**, 342.

7. U. S. P. 1016476, 1912; abst. C. A. 1912, **6**, 796.

8. U. S. P. 1028880, 1912; abst. C. A. 1912, **6**, 2499; Chem. Ztg. Rep. 1912, **36**, 405; Mon. Sci. 1912, **77**, 133.

9. U. S. P. 1113437, 1914; abst. C. A. 1914, **8**, 3842; Chem. Ztg. Rep. 1915, **39**, 20.

form, or of iron oxide. Numerous other catalysts have, however, been proposed. The platinum and iron oxide catalysts are described in detail in later sections, but the other catalytic masses which have been proposed may be noticed in this place. A comprehensive list of catalysts include:

(1) Platinum in the form of platinized asbestos or ferric oxide, platinum sponge, and, in the Schroder-Grillo process, platinized magnesium sulfate.

(2) Oxides and sulfates of iron, chromium,¹ nickel, cobalt, manganese, uranium, vanadium,² titanium,³ ferro-titanium,⁴ and copper.

(3) Oxygen compounds of aluminium, beryllium, zirconium, cerium and didymium.

(4) Mixtures of (2) and (3), and of (1) with (2) and (3).

(5) Ultraviolet light,⁵ or radioactive material.⁶

(6) Electrical discharges,⁷ or contact masses electrically heated.⁸

Methods of promoting efficient mixing of the gases proceeding to the contact mass have been described by R. Knietsch.⁹ The

1. A. Matignon et al, E. P. 8102, 1908. F. P. 376629, 1907. A. Clascen, D. R. P. 274345. A. Clemm, W. Hasenbach and Verein Chem. Fabr. Mannheim, U. S. P. 729735. E. P. 4610, 1901. Badische Anilin u. Sodafabrik, E. P. 10729, 1901. C. Ellis, U. S. P. 1204141, 1204142, 1204143, 1227044. E. P. 110776, 1916. Can. P. 177145, 186962.

2. Zts. anorg. Chem. 1905, 453. Badische Anilin u. Sodafabrik, E. P. 23541, 1913; abst. J. S. C. I. 1915, **34**, 833; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 112. D. R. P. 291792, 1913; abst. C. A. 1917, **36**, 1024. Norw. P. 27449, 1916; cf. F. Fahrenwald, Bull. Amer. Inst. Min. Eng.; abst. Chem. Trade J. Jan. 6, 1917; J. S. C. I. 1917, **36**, 81. H. v. Keler and A. Weindel, U. S. P. 1102670; F. P. 460074, abst. J. S. C. I. 1914, **33**, 22, 831. Can. P. 190755, 1919; abst. C. A. 1919, **13**, 1747. Soc. Anon. Conidelon, E. P. 5174, 1913. D. R. P. 266190; abst. J. S. C. I. 1913, **32**, 791. Farb. vorm. F. Bayer & Co., E. P. 15165, 1913. D. R. P. 280960. F. P. 460014; abst. Mon. Sci. 1914, **81**, 74. E. P. 8545, 1901; abst. J. S. C. I. 1902, **31**, 475. U. S. P. 687834.

3. P. Farup, E. P. 454893; abst. Mon. Sci. 1914, **77**, 10.

4. P. Farup, E. P. 5079, 1913. D. R. P. 263392. Norw. P. 22895. U. S. P. 1219288. Abst. C. A. 1917, **11**, 1526. J. S. C. I. 1913, **32**, 867; 1917, **36**, 457.

5. A. Coehn and H. Becker, D. R. P. 217722, 1907; abst. C. A. 1910, **4**, 1531.

6. W. Hallock, U. S. P. 930471, 1909; abst. Mon. Sci. 1910, **73**, 81.

7. E. Riesenfeld, D. R. P. 229274. I. Kitsee, U. S. P. 869094. H. Kühne, E. P. 17520, 1908. F. Cottrell, E. P. 21147, 1907. C. Jacobs, U. S. P. 704831, 1902. B. Bradley, E. P. 16152, 1911.

8. C. Brockbank, U. S. P. 1157293; abst. J. S. C. I. 1915, **34**, 1197.

9. U. S. P. 688020, 1901; abst. Chem. Zts. 1902, **1**, 479; J. A. C. S. 1902, **24**, 261; Mon. Sci. 1902, **58**, 71. U. S. P. 688469, 1901; abst. J. A. C. S. 1902, **24**, 262; Mon. Sci. 1902, **58**, 72. U. S. P. 688470, 1901; abst. J. A. C. S. 1902, **24**, 262; Mon. Sci. 1902, **58**, 72.

gas is usually led through a number of small pipes containing the contact body.

The problem of the absorption of the product of reaction is one of great importance. If it is attempted to absorb the sulfur trioxide in water, a fine mist of fog of sulfuric acid droplets is formed, which is only with the greatest difficulty absorbed by water. It has been inferred that this is due to a peculiar vesicular constitution of the droplets, but there is no evidence to believe that the property is due to other than the surface tension effect of the small droplets, and also to electrostatic charges upon them which prevent their coalescing or forming liquid in bulk. This property is frequently observed with wet vapors, and if these are dried the droplets usually coapt. This has been used in the present case by passing the gas containing sulfur trioxide directly into strong sulfuric acid, when absorption readily occurs. G. Stone¹ passes the gas through a cooled tower, down which dilute sulfuric acid trickles, the tower containing tubes. The use of dilute acid appears not to be of advantage. In the process of J. Herreshoff,² which has been largely used, the gas is passed into 90% sulfuric acid, and the latter maintained at a constant strength by the regulated addition of water. In the method of R. Knietzsch,³ the sulfur trioxide is absorbed in oleum containing at least 27% free SO₃, which does not attack iron. M. Schroeder⁴ prefers dilute acid in a tower, to bring about intimate contact. It would appear, however, that irrespective of the efficiency in mixing, fog is produced, and all proposals to use dilute acid or water must be regarded as retrograde steps. It is true that the mist may afterwards be thrown down by electrostatic precipitation,⁵ but the absorption in strong acid seems to offer a preponderance of advantages. The distribution of the absorbing me-

1. U. S. P. 695180, 1902; abst. Chem. Zts. 1903, **2**, 9; J. A. C. S. 1902, **24**, 431; Mon. Sci. 1902, **58**, 184.

2. U. S. P. 722981, 1903; abst. Chem. Zts. 1903, **2**, 477; J. A. C. S. 1903, **25-R**, 491. U. S. P. 737625, 737626, 1903; abst. Chem. Zts. 1904, **3**, 117, 291; J. A. C. S. 1904, **26-R**, 190; Mon. Sci. 1903, **59**, 183.

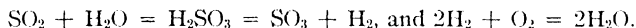
3. U. S. P. 800218, 1905; abst. J. A. C. S. 1905, **27-R**, 232; Mon. Sci. 1906, **65**, 19. U. S. P. 816918, 1906; abst. J. A. C. S. 1906, **28-R**, 520; Mon. Sci. 1906, **65**, 116. Cf. H. Weber, U. S. P. 1233627; abst. C. A. 1917, **11**, 2601.

4. U. S. P. 789634, 1905; abst. Chem. Zts. 1905, **4**, 303, 386; J. A. C. S. 1906, **28-R**, 46.

5. F. Cottrell, U. S. P. 866843, 866844, 1907; abst. Chem. Ztg. Rep. 1907, **31**, 562; Mon. Sci. 1908, **69**, 49.

dium over the walls of a number of chambers, in order to expose a larger surface, has also been described;¹ however, this is unnecessary with strong acid, when simple iron towers answer the purpose. The temperature of the acid may be reduced, either externally by a cooler,² or by allowing cold water to flow over the walls of the absorption chamber.³

Platinum Catalysts. According to G. Lunge,⁴ 1 kgm. of platinum in the form of platinized asbestos, should produce in a satisfactory process from 600 to 700 kgm. SO_3 per 24 hours. The action of the catalyst may consist in the production of an intermediate oxide, which is alternately formed and reduced, although H. Wieland⁵ suggests that the presence of moisture is necessary, and that the reaction is



This theory seems highly improbable. The catalytic action of platinum in the process has also been investigated by a number of experimenters.⁶

The particular physical form in which the platinum is used varies considerably. The preparation of active platinized asbestos has been described by C. Winkler.⁷ In general, the asbestos is washed with strong hydrochloric acid, and thoroughly soaked in a solution of platinum chloride made alkaline with soda and mixed with sufficient sodium formate solution to reduce the

1. H. Eschellmann and A. Harmuth, U. S. P. 894792, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 452.

2. I. Cox, U. S. P. 1002824, 1911; abst. C. A. 1911, **5**, 3911; Chem. Ztg. Rep. 1911, **35**, 545.

3. T. Briggs and H. Merriam, U. S. P. 1013638, 1912; abst. C. A. 1912, **6**, 671; Chem. Ztg. Rep. 1912, **36**, 194; Mon. Sci. 1912, **77**, 130. U. S. P. 1082301, 1913; abst. C. A. 1914, **8**, 792; Mon. Sci. 1914, **81**, 65. Other processes are: H. Deacon, E. P. 1908, 1871. O. Dieffenbach, E. P. 26537, 1901. L. Bassett, Swiss P. 74444, 1917; abst. C. A. 1918, **12**, 83. W. Ferguson, E. P. 6824, 1903. H. Blackmore, E. P. 27907, 1904. J. Starek, E. P. 12028, 1889. L. Bassett, E. P. 100597, 1916; abst. C. A. 1916, **10**, 2505. R. Marot, E. P. 14372, 1904. G. Lunge, E. P. 3166, 1888. G. Lunge and C. Göpner, E. P. 1523, 1878.

4. G. Lunge, "Sulfuric Acid and Alkali," 4th ed.

5. Ber. 1912, **45**, 685.

6. P. Wenger and C. Urfer, Ann. Chim. Anal. 1918, **23**, 97; abst. C. A. 1918, **12**, 1864; J. S. C. I. 1918, **37**, 368-A. R. Knietsch, Ber. 1901, **34**, 4069. G. Bodländer and W. Pohl, Zts. Elektrochem. 1905, **11**, 373. M. Bodenstein and C. Fink, Zts. physik. Chem. 1907, **60**, 46. R. Lucas, Zts. Elektrochem. 1905, **11**, 457.

7. D. R. P. 4566, 1878; abst. J. A. C. S. 1879, **1**, 300; Chem. Zts. 1902, **1**, 13; Wag. Jahr. 1879, **25**, 284.

platinum. This may conveniently be carried out in a porcelain sink with a flat bottom, the pasty mixture being dried on a water bath, when platinum separates in a finely divided black form, closely adhering to the asbestos fiber, the salts being removed by washing with water. A similar method may be used to impregnate the asbestos mats used in the Tentelew process; these are washed, dried and stored for use in dust-free cupboards. The amount of platinum used varies with the nature of the process. In the platinized mats, of cross-section 3 ft. by 2 ft., each contains about 40 gms. of platinum.

It would appear that in some processes platinized pumice is used. This may be prepared in a similar way to platinized asbestos, but J. Partington (private communication) finds that in a number of catalytic reactions pumice, if used as a support, acts as a decided anti-catalyst. Other methods of precipitating the platinum have been described.¹

P. Sabatier and A. Mailhe² use a network of wires of the massive metal, while platinized platinum foil may also be employed. Inactive supports have been proposed, such as mica,³ meerschaum, clay,⁴ aluminium oxide,⁵ quartz or porcelain, the

1. M. Neumann, D. R. P. 188503; abst. Zts. ang. Chem. 1908, **21**, 795; Chem. Zentr. 1907, **78**, 11, 1948; Jahr. Chem. 1905-1908, **1**, 3244; Chem. Ztg. Rep. 1907, **31**, 534; Wag. Jahr. 1907, **53**, **1**, 574; Mon. Sci. 1910, **73**, 66. D. R. P. 218725; abst. Zts. ang. Chem. 1910, **23**, 1053; Chem. Zentr. 1910, **81**, **1**, 875; Jahr. Chem. 1910, **63**, **1**, 989; Chem. Ztg. Rep. 1910, **34**, 125; Wag. Jahr. 1910, **56**, **1**, 602; Mon. Sci. 1913, **79**, 158. A. Carey, O. Heslop and The United Alkali Co., E. P. 10351, 1902; abst. J. S. C. I. 1903, **22**, 553; Chem. Ztg. 1903, **27**, 880. H. Neuendorf, D. R. P. 127846, 1899; Zts. ang. Chem. 1902, **15**, 162; Chem. Centr. 1902, **73**, **1**, 504; Jahr. Chem. 1902, **55**, 232; Chem. Zts. 1902, **1**, 450, 474; Chem. Ztg. 1902, **26**, 164; Wag. Jahr. 1902, **48**, **1**, 297; Mon. Sci. 1902, **58**, 181. W. Porter, U. S. P. 612614, 1898. Chem. Fabrik. Griesheim-Elektron, U. S. P. 971149; abst. Chem. Ztg. Rep. 1910, **34**, 610; Mon. Sci. 1913, **79**, 100. O. Niedenführ, D. R. P. 225705; abst. C. A. 1911, **5**, 1171; Zts. ang. Chem. 1910, **23**, 2190; Chem. Zentr. 1910, **81**, **11**, 1007; Jahr. Chem. 1910, **63**, **1**, 989; Chem. Ztg. Rep. 1910, **34**, 467; Wag. Jahr. 1910, **56**, **1**, 421; Mon. Sci. 1914, **81**, 87. W. Majert, D. R. P. 134928; abst. Zts. ang. Chem. 1902, **15**, 1098; Chem. Centr. 1902, **73**, **11**, 1022; Jahr. Chem. 1902, **55**, 232; Chem. Zts. 1903, **2**, 275; Chem. Ztg. 1902, **26**, 936; Wag. Jahr. 1902, **48**, **1**, 296. R. Langhans, D. R. P. 134738; abst. Jahr. Chem. 1902, **55**, 514; Chem. Zts. 1903, **2**, 281; Chem. Ztg. 1902, **26**, 1180; Wag. Jahr. 1902, **48**, **1**, 265. Goldenberg, Geromont & Co., E. P. 618, 1900; abst. J. S. C. I. 1901, **20**, 250.

2. E. P. 2011, 1915.

3. A. de Montlaur, D. R. P. 267868; abst. C. A. 1914, **8**, 1491; Zts. ang. Chem. 1914, **27**, 61; Chem. Zentr. 1914, **85**, **1**, 197; Chem. Ztg. Rep. 1914, **38**, **8**; Wag. Jahr. 1913, **59**, **1**, 500.

4. O. Efrem and J. Klaudy, E. P. 14339, 1899.

5. Spencer, Kellogg & Sons, U. S. P. 1111502; abst. C. A. 1914, **8**, 3635; Chem. Ztg. Rep. 1915, **39**, 47; Mon. Sci. 1914, **81**, 179.

material afterwards being heated till the platinum softens.¹ Except in the latter case (glazed porcelain), Partington finds a diminution in catalytic activity due to the anti-catalytic action of the support.

The use of a hollow perforated metal support has been described,² cast-iron, copper, aluminium or zinc being regarded as suitable. The use of iron oxide or oxides of chromium or copper, or mixtures of these, has also been advocated.³ M. Schroeder⁴ dissolves a mixture of platinum chloride and another soluble salt in water, evaporates to dryness, and heats to decompose the platinum, a suitable salt being magnesium sulfate.

The Badische Co.⁵ point out that the catalytic efficiency of the platinum is counteracted by the reverse action of the SO_3 produced, and propose to work in two or more stages, 80% to 90% of the SO_2 being changed into SO_3 in the first apparatus and absorbed, and the remainder converted in the succeeding apparatus. In this way an economy of platinum is claimed. Eschellmann and Harmuth also pass the gases first through a thick layer of platinized asbestos, then through a perforated plate, and finally through 25 layers of platinized asbestos.⁶ W. Hasenbach⁷ uses a plurality of sheets of platinized fabric.

A loss of platinum appears to occur in the contact process,⁸ equivalent to about 1 grain per ton of acid produced. It is supposed that this occurs mechanically, and Partington states that in other catalytic reactions the surface of the platinum becomes

1. Chem. Fabrik. Griesheim-Elektron, F. P. 380884, 1907.

2. O. Nidenführ, D. R. P. 225705, 1908; abst. C. A. 1911, **5**, 1174; Zts. ang. Chem. 1910, **23**, 2190; Chem. Zentr. 1910, **81**, II, 1007; Jahr. Chem. 1910, **63**, I, 989; Chem. Ztg. Rep. 1910, **34**, 467; Wag. Jahr. 1910, **56**, I, 421; Mon. Sci. 1914, **81**, 87.

3. A. Clemm and W. Hasenbach, U. S. P. 690133, 1901; abst. Chem. Zts. 1902, **1**, 580; J. A. C. S. 1902, **24**, 338; Mon. Sci. 1902, **58**, 73. Badische Anilin u. Sodafabrik, E. P. 10729, 1901; abst. J. S. C. I. 1902, **21**, 548; Chem. Ztg. 1902, **26**, 929; Mon. Sci. 1903, **59**, 75. D. R. P. 140353, 1901; abst. J. S. C. I. 1903, **22**, 553; Zts. ang. Chem. 1903, **16**, 352; Chem. Centr. 1903, **74**, I, 940; Jahr. Chem. 1903, **56**, 345; Chem. Zts. 1903, **2**, 648; Chem. Ztg. 1903, **27**, 393; Wag. Jahr. 1903, **49**, I, 250.

4. U. S. P. 636924, 1899.

5. E. P. 12781, 1901; abst. J. S. C. I. 1902, **21**, 772; J. Soc. Dyers Col. 1902, **18**, 197.

6. G. Eschellmann and A. Harmuth, U. S. P. 1030508, 1036473, 1912; abst. C. A. 1912, **6**, 2500, 3315; Chem. Ztg. Rep. 1912, **36**, 662; 1913, **37**, 32.

7. U. S. P. 752165, 1904; abst. J. A. C. S. 1904, **26R**, 405; Mon. Sci. 1905, **63**, 7.

8. R. Messel, Chem. Trade J. 1912, **51**, 237.

spongy, and minute pieces of metal are carried off by the current of gas. As a catalyst, the metal is most active when its surface has assumed the spongy condition.

Methods of revivifying the contact mass have been described. If it has been rendered inactive by arsenic, the latter may be removed by mixing steam with the gases,¹ or hydrochloric acid gas may be used, or ammonium chloride, sulfur chloride, sulfuryl chloride, phosgene, a halogen substituted hydrocarbon, or an acid chloride.²

Oxide of Iron Catalysts. The use of oxide of iron as a catalyst for the conversion of SO_2 into SO_3 was the subject of an English patent granted to W. Hunt in 1853.³ In 1852 Wöhler described the catalytic activity of oxides of iron, copper and chromium in connection with the conversion of SO_2 into SO_3 , and the subject has been investigated by G. Lunge and others.⁴ The problem was further elucidated by W. Hasenbach⁵ and A. Clemm,⁶ and by these two chemists in conjunction,⁷ on behalf of the Verein Chemischer Fabriken of Mannheim, by whom the process was developed on a manufacturing scale.⁸ The result of this work

1. Farbwerke vorm. Meister, Lucius & Brüning, E. P. 4026, 1902; abst. J. S. C. I. 1903, **22**, 93. Cie. Parisienne de Coul. d'Aniline, F. P. 318861, 1902; abst. J. S. C. I. 1902, **21**, 1454.

2. Badische Anilin u. Sodafabrik, D. R. P. 148196; Zts. ang. Chem. 1904, **17**, 244; Chem. Centr. 1904, **75**, I, 413; Jahr. Chem. 1904, **57**, 460; Chem. Ztg. 1904, **28**, 65; Wag. Jahr. 1904, **50**, I, 289; Chem. Zts. 1904, **3**, 460, 504. E. P. 20915, 1902; F. P. 324751, 1902; abst. J. S. C. I. 1903, **22**, 628; 950. Badische Anilin u. Sodafabrik, Aust. P. 16116, 1903; abst. Chem. Zts. 1904, **3**, 667. W. Kelsey and the New Jersey Zinc Co., U. S. P. 1047236; abst. C. A. 1913, **7**, 685; Chem. Ztg. Rep. 1913, **37**, 198; Mon. Sci. 1913, **79**, 99.

3. E. P. 1919, 1853.

4. Ann. 1852, **81**, 255; see also G. Lunge, Ber. 1877, **10**, 1824; Chem. Ztg. 1883, **7**, 29; Zts. ang. Chem. 1900, **80**. G. Lunge and G. Pollitt, Zts. ang. Chem. 1902, **15**, 1105; abst. J. S. C. I. 1902, **21**, 1329. U. S. P. 758844, 1904. G. Keppeler, J. S. C. I. 1902, **21**, 1137. G. Lunge and K. Reinhardt, J. S. C. I. 1904, **23**, 821. F. Küster, J. S. C. I. 1904, **23**, 982.

5. U. S. P. 670559, 1901; abst. Mon. Sci. 1901, **57**, 154; 281. U. S. P. 681698, 1901.

6. U. S. P. 716985, 1902; E. P. 15151, 1899; abst. J. S. C. I. 1900, **19**, 442; 1903, **22**, 145. Cf. G. Lunge and G. Pollitt, J. S. C. I. 1903, **22**, 79.

7. A. Clemm and W. Hasenbach, U. S. P. 690133, 1901; abst. J. S. C. I. 1902, **21**, 254. U. S. P. 716985; abst. J. S. C. I. 1903, **22**, 145. U. S. P. 729735, 1903; abst. J. S. C. I. 1903, **22**, 795. E. P. 17266, 1898; abst. J. Soc. Dyers Col. 1899, **15**, 241; Mon. Sci. 1900, **56**, 117. In this connection, compare W. Majert, E. P. 256, 1878; J. and W. Allen, E. P. 1094, 1858.

8. Ver. Chem. Fabr. in Mannheim, Removal of arsenic from burner gases, D. R. P. 106715. E. P. 17266, 1898. Aust. P. 484. F. P. 280393. Belg. P. 137510; abst. Wag. Jahr. 1899, **45**, 356. Production of SO_3 , D. R.

was the definite establishment of the following facts:

(1) When the temperature of the contact mass is maintained at about 600° , approximately 60% of the SO_2 is converted into SO_3 .

(2) The gases going to the contact mass must be dried by passing through strong sulfuric acid, or preferably the air used in the pyrites burners must be dried in this way, and no other moist air allowed to pass into the burners.

(3) The whole of the arsenic in the burner gas is removed by passage through the iron oxide so that the unconverted residue of SO_2 may be passed to a platinum catalyst without danger of poisoning the latter.

The Mannheim process has been extensively used, in most cases in connection with some form of platinum catalyst for completing the conversion, and has been found satisfactory. In British practice, however, it has been found more expensive than the Grillo process, and is not so much favored. Gas containing 2%-3% SO_2 is produced from pyrites in special burners, covered with sheet-iron to prevent the entrance of moist air, dried in a sulfuric acid tower being used. The gases pass from four burners arranged in a square to a shaft (Fig. 91), containing burnt pyrites, the material being fed in at the top and removed from time to time at the bottom. The temperature in the shaft is maintained at about 600° , the gases being cooled and passed into sheet iron towers containing strong sulfuric acid to absorb the SO_3 . The exit gases may then pass to coke scrubbers to filter out acid mist, to a re-heater, and then to a platinum catalyst, say

P. 107995. E. P. 17266, 1898. Aust. P. 484. F. P. 280393. Belg. P. 137510. U. S. P. 681698. Swiss P. 18187, 1899. Pyrites burner, D. R. P. 108445; E. P. 1859, 1899. Aust. P. 2159. F. P. 285459. Belg. P. 140695, 140696. U. S. P. 670559; abst. Wag. Jahr. 1900, **46**, i, 318. Method of operating pyrites burners, D. R. P. 108446. E. P. 3185, 1899. Aust. P. 483. F. P. 280393 and additions thereto. Belg. P. 140695. Combination of an iron oxide and platinum catalytic process, D. R. P. 136134. E. P. 24748, 1899. Aust. P. 10510. F. P. 295238 and additions thereto. Belg. P. 147437, 155501. U. S. P. 690133. Copper or chromium oxide catalyst, D. R. P. 142410. E. P. 4610, 1901. Aust. P. 10511. F. P. 295238 and additions thereto. Belg. P. 155501. Contact oven, comprizing the use of platinum catalyst, D. R. P. 142855. E. P. 16206, 1902. Aust. P. 15339. F. P. 323491. Belg. P. 164891. U. S. P. 752165; abst. Wag. Jahr. 1903, I, 256. Use of arsenical iron oxide as a catalyst, D. R. P. 154084. Aust. P. 484. F. P. 280393. Belg. P. 137510. Use of copper sulfate for the production of SO_3 , E. R. 15151, 1899. U. S. P. 716985. See also D. R. P. 108446. D. R. P. 136134. E. P. 24748, 1899. D. R. P. 154084. W. Wilke, J. S. C. I. 1906, **25**, 4. Aust. P. 65943; abst. Oest. Chem. Ztg. 1917, **20**, 14.

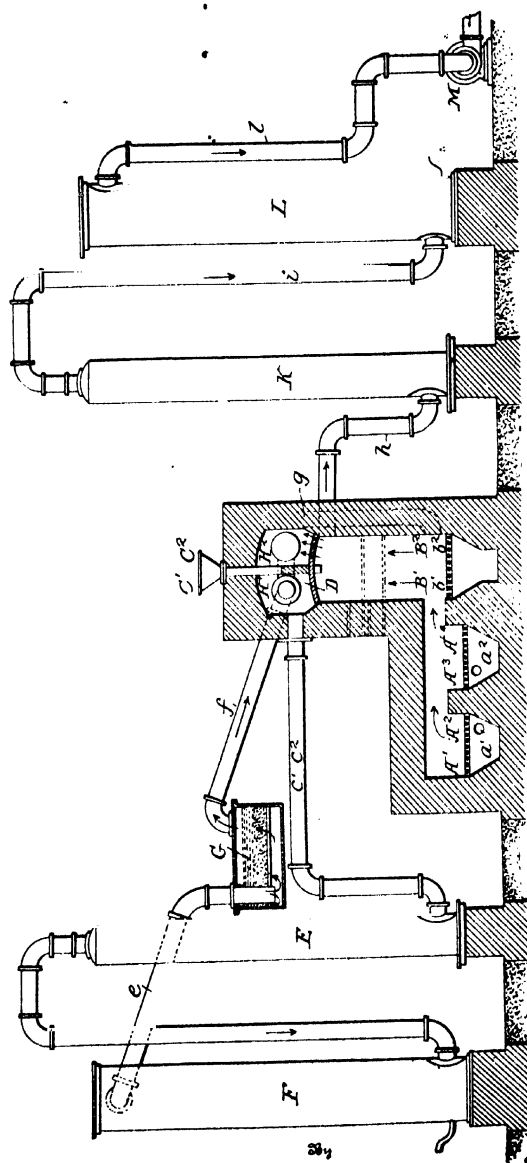


FIG. 91.—THE CLEMM AND HASENBACH PROCESS OF SULFURIC ANHYDRIDE MANUFACTURE

of asbestos mats impregnated with platinum arranged in an iron frame stretching across a flue, to complete the conversion.¹

Modifications of the iron oxide process are numerous. It has been proposed to blow the finely divided oxide of iron into the gases by means of a fan or otherwise,² when less catalyzer is said to be required than with a stationary mass. It is difficult to see what advantage this could have with such a cheap catalyzer as iron oxide. The use of mixtures of iron oxide with oxides of the alkaline-earth metals, as lime or strontia, have been proposed.³ A catalyst composed of alundum particles 40 parts, copper oxide 9 parts, and silica 0.7 part is described by J. Beckman⁴ oxides of chromium are also referred to,⁵ while the use of ferric oxide prepared from bauxite or bog iron ore is said⁶ to possess advantages. Experiments on the use of roasted pyrites as a contact agent for the oxidation of undried smelter gas have been made by T. Smith.⁷ Numerous modifications of the iron oxide process⁸ appear to offer nothing fundamentally new.

Chromium Catalysts. The use of chromium sesquioxide as a catalyst has already been mentioned in connection with iron

1. H. Ditz and F. Kanhäuser, *Zts. ang. Chem.* 1918, **31**, 149, 153; abst. *J. S. C. I.* 1918, **37**, 577-A; *C. A.* 1919, **13**, 1128.
2. E. Taylor and F. Bergh, *U. S. P.* 1157455, 1915; abst. *J. S. C. I.* 1916, **35**, 175; *C. A.* 1915, **9**, 3335; *Mon. Sci.* 1916, **83**, 37. J. McFetridge, *U. S. P.* 988646; abst. *C. A.* 1911, **5**, 2158; *Mon. Sci.* 1912, **77**, 19.
3. K. Albert, *U. S. P.* 1018402, 1912; abst. *J. S. C. I.* 1912, **31**, 334; *Mon. Sci.* 1912, **77**, 132. D. R. P. 238371, 1910; abst. *C. A.* 1912, **31**, 1663; *Zts. ang. Chem.* 1911, **24**, 2030; *Chem. Zentr.* 1911, **82**, II, 1078; *Chem. Zts.* 1912, **11**, No. 2787; *Zts. Schiess. Spreng.* 1911, **6**, 411; *Chem. Ztg. Rep.* 1911, **35**, 503; *Wag. Jahr.* 1911, **57**, I, 421.
4. *U. S. P.* 1007516, 1911; abst. *C. A.* 1912, **6**, 36; *Chem. Ztg. Rep.* 1912, **36**, 105; *Mon. Sci.* 1912, **77**, 156.
5. A. Maignon, R. Tramoy, E. Urbain, A. Feige, A. Verley, *E. P.* 8102, 1908; abst. *J. S. C. I.* 1908, **27**, 910.
6. H. Fritzweiler, B. Stuer and Chem. Fabr. Rhénania, *E. P.* 109056, 1917; abst. *J. S. C. I.* 1918, **37**, 506-A; *Mon. Sci.* 1919, **86**, 34.
7. T. Smith, *Chem. Eng.* 1909, **9**, 37; abst. *C. A.* 1909, **3**, 1204.
8. H. Frasch, *U. S. P.* 664630, 1900; abst. *Chem. Ztg.* 1901, **25**, 50. V. Ragsine and P. Dvorkovitch, *E. P.* 12700, 1887. L. Bassett, *U. S. P.* 1197331; abst. *C. A.* 1916, **10**, 2967. *Can. P.* 192662; abst. *C. A.* 1919, **13**, 2742. H. Blackmore, *U. S. P.* 686021, 686022, 1901; *E. P.* 11995, 1902; abst. *J. S. C. I.* 1902, **21**, 914. H. Hilbert, *E. P.* 9453, 1903; *Belg. P.* 169912, 1903. Bayer, A. G. Henfeld, D. R. P. 163835; 179588. C. Krauss and R. von Berneck, *U. S. P.* 700512, 1902. H. Briegleb, *E. P.* 11792, 1901; D. R. P. 121906, 1900. *Belg. P.* 157003, 1901. I. Lihme, *U. S. P.* 1103522, 1914; abst. *J. S. C. I.* 1914, **33**, 919. A. Sebillot and L. Maclaure, *E. P.* 2192, 1909. T. Wrampelmeier, *U. S. P.* 948947; abst. *C. A.* 1910, **4**, 1090. W. Alcock and G. Davis, *E. P.* 16981, 1915; abst. *J. S. C. I.* 1917, **36**, 82. W. Hasenbach, *U. S. P.* 681698, 1901. H. Nishida, *Jap. P.* 31972; abst. *C. A.* 1918, **12**, 2238.

oxide. Its activity depends largely on its method of preparation. Generally speaking, it may be said that chromium oxide for use as a catalyst should be prepared at a low temperature, as the oxide which has been ignited is much less active than that made by precipitation and gentle heating. A porous oxide is prepared by the ignition of ammonium bichromate or chromium nitrate.¹ Metallic chromium, or its alloys with vanadium, and iron or alloys of iron, and molybdenum, or with silicon and manganese, or silicon, manganese and aluminium, have been proposed.² The Verein Chemischer Fabriken of Mannheim³ describe oxide of chromium impregnated with platinum, as well as copper and iron oxides with platinum. C. Ellis⁴ has patented a mixture of chromium oxide with a tin compound, whereby tin chromate or chromium stannate is formed. Instead of tin, lead, antimony, bismuth or cadmium oxides may be used, as when a mixture of ammonium bichromate and antimony chloride is ignited.

Chromium oxide obtained by the ignition of ammonium bichromate is very voluminous and dusty, but may be compressed into pastilles without losing its activity, whereas the denser oxide obtained by the ignition of chromium nitrate is much less active.

Titanium Catalysts. The use of titanium as a catalyst, usually associated with iron as the mineral ilmenite, FeTiO_3 , has been proposed by P. Farup.⁵ The mineral is treated with concentrated sulfuric acid (1 to 2 times the weight of the ilmenite), and heated, when it swells up, and yields a porous mass, which is then heated to $700^\circ\text{--}900^\circ$ to drive off sulfuric acid.

Vanadium Compounds as catalysts for the conversion of

1. A. Matignon, R. Trannoy, E. Urbain, A. Feige and A. Verley, E. P. 8102, 1908. F. P. 376629, 1907; abst. J. S. C. I. 1907, **26**, 1008; 1908, **27**, 940. Belg. P. 207249, 1908.

2. A. Classen, D. R. P. 274345, 1913; abst. J. S. C. I. 1914, **33**, 788.

3. A. Clemm, W. Hasenbach and Verein Chemischer Fabr. in Mannheim, U. S. P. 729735; E. P. 4610, 1901; abst. J. S. C. I. 1902, **21**, 253; 1903, **22**, 795. Badische Anilin u. Sodafabrik, E. P. 10729, 1901; abst. J. S. C. I. 1902, **21**, 548.

4. C. Ellis and H. Weber, U. S. P. 1204141, 1204142, 1204143, 1915; abst. J. S. C. I. 1916, **35**, 1260. U. S. P. 1227044, 1917; abst. J. S. C. I. 1917, **36**, 711. C. Ellis, E. P. 110776, 1916; abst. C. A. 1918, **12**, 518; J. S. C. I. 1917, **36**, 1272. Can. P. 177145, 186962, 1917; abst. C. A. 1918, **12**, 83, 2667; U. S. P. 1314952; abst. C. A. 1919, **13**, 2742; J. S. C. I. 1919, **38**, 817-A.

5. P. Farup, E. P. 5079, 1913. D. R. P. 263302. F. P. 454893. Norw. P. 22895. U. S. P. 1219288. Abst. C. A. 1917, **11**, 1526; J. S. C. I. 1913, **32**, 867; 1917, **36**, 457. Belg. P. 254287, 1913.

SO_2 into SO_3 have been investigated by J. Küster and Franke,¹ who state that vanadium pentoxide acts similarly to ferric oxide, but is more permanently active. The Badische Co.² also propose the use of vanadium compounds spread on a finely divided indifferent carrier such as finely ground pumice, the granules of which have a diameter not exceeding 20 microns (0.002 cm.). Thus, pumice is mixed with ammonium vanadate and heated, first in air to drive off ammonia and then in gases containing sulfur dioxide to activate the catalyst. Or kieselguhr or precipitated silica may be combined with a solution of a vanadate, and the mixture granulated and treated as before. Silver vanadate may be used.³ Other methods of preparation have been described by Soc. Anon. Conidelon,⁴ and Farbenfabriken vorm. F. Bayer and Co.⁵ The latter employ a mixture of vanadium pentoxide and silver vanadate. E. de Haen⁶ has described a similar process, a mixture of air and SO_2 being passed over asbestos impregnated with V_2O_5 . H. v. Keler and A. Weindel propose the use of a silver vanadium compound.⁷

Radioactive Catalysts. The use of radioactive catalysts has already been referred to.⁸ They appear unlikely to be useful on a technical scale.

Other Catalysts have been proposed, but there is no information indicating whether these have ever been practically used,

1. Zts. anorg. Chem. 1905, **42**, 453; abst. Chem. Centr. 1905, **76**, I, 328.
2. Badische Anilin u. Sodafabrik, E. P. 23541, 1913; abst. J. S. C. I. 1915, **34**, 833; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 112. D. R. P. 291792, 1913; abst. C. A. 1917, **36**, 1024; Zts. ang. Chem. 1916, **29**, 270; Chem. Zentr. 1916, **87**, I, 1048; Chem. Ztg. Rep. 1916, **40**, 211. Norw. P. 27449, 1916; abst. C. A. 1917, **11**, 526. Cf. F. Fahrenwald, Bull. Amer. Inst. Min. Eng., abst. Chem. Trade J. Jan. 6, 1917; J. S. C. I. 1917, **36**, 81.
3. H. v. Keler and A. Weindel, U. S. P. 1102670; E. P. 460074; abst. J. S. C. I. 1914, **33**, 22, 831. Can. P. 190755, 1919; abst. C. A. 1919, **13**, 1747.
4. Soc. Anon. Conidelon, E. P. 5174, 1913, D. R. P. 266190; abst. J. S. C. I. 1913, **32**, 791.
5. Farb. vorm. F. Bayer & Co., E. P. 15165, 1913. D. R. P. 280960. E. P. 460014; abst. Mon. Sci. 1914, **81**, 74. Belg. P. 258157, 1913.
6. E. P. 8545, 1901; abst. J. S. C. I. 1902, **31**, 475. U. S. P. 687834. Belg. P. 156195, 1901. Cf. A. Heimrod and H. Egbert, Chem. Trade J. Feb. 15, 1919; Chem. Met. Eng. 1918, **19**, 309; abst. C. A. 1919, **13**, 501.
7. Can. P. 190755, 1920.
8. A. Coehn and H. Becker, D. R. P. 217722, 1907; abst. C. A. 1910, **4**, 1591; Zts. ang. Chem. 1910, **23**, 764; Chem. Zentr. 1910, **81**, I, 585; Jahr. Chem. 1910, **63**, I, 526; Chem. Ztg. Rep. 1910, **34**, 50; Wag. Jahr. 1910, **56**, I, 419; Zts. Schiess. Spreng. 1910, **5**, 53; Mon. Sci. 1913, **79**, 158. W. Hallock, U. S. P. 930471, 1909; abst. Mon. Sci. 1910, **73**, 81.

and if so, with what results. The employment of copper salts has already been mentioned.¹ C. Ellis proposes the use of selenium and tellurium compounds;² arsenic pentoxide, according to Lunge and Reinhardt, although the trioxide acts as a catalyst poison;³ while other proposals deal with phosphoric acid on asbestos,⁴ nickel,⁵ metals of the tantalum group,⁶ ferrosilicon,⁷ various alloys,⁸ rare earths such as oxides of cerium, lanthanum, yttrium and thorium,⁹ beryllia, alumina, zirconia, etc., with oxides of iron, nickel and chromium,¹⁰ together with other mixed catalysts of which it is difficult to form a clear idea of the composition.¹¹ The use of calcium sulfate,¹² and of ozone,¹³ has been recorded.

Electrical Processes. The production of sulfuric acid by the action of the electric discharge on mixtures of sulfur dioxide and

1. A. Clemm, U. S. P. 716985, 1902; abst. Chem. Zts. 1903, **2**, 375; J. A. C. S. 1903, **25R**, 344; Mon. Sci. 1903, **59**, 100. H. Deacon, E. P. 2641, 1870; 753, 1871; 3669, 1888.
2. U. S. P. 1103017, 1914; abst. J. S. C. I. 1914, **33**, 864; C. A. 1914, **8**, 3101; Zts. ang. Chem. 1916, **29**, 1, 116; Mon. Sci. 1914, **81**, 178. See G. Lunge and K. Reinhardt, J. S. C. I. 1904, **23**, 821.
3. E. Opl. Chem. Ztg. 1905, **29**, 757; abst. Jahr. Chem. 1905-1908, 1, 1618.
4. Cie. Par. de Coul. d'Aniline, F. P. 318770, 1902; abst. J. S. C. I. 1902, **21**, 1453; Chem. Zts. 1903, **2**, 274; Mon. Sci. 1903, **59**, 122.
5. G. Schicht, Akt. Ges., Aust. P. 70771. A. Wells, U. S. P. 1179184; abst. J. S. C. I. 1916, **35**, 623; Chem. Ztg. Rep. 1917, **41**, 123.
6. Bonhard & Loyer, F. P. 321573, 1902; abst. J. S. C. I. 1903, **22**, 212; Chem. Zts. 1903, **2**, 529.
7. A. v. Grätzel, E. P. 7452, 1904; abst. J. S. C. I. 1905, **24**, 332.
8. E. Anderson, E. P. 7839, 1913. F. P. 457569; abst. C. A. 1914, **8**, 2040, 3223; J. S. C. I. 1914, **33**, 470; Chem. Ztg. Rep. 1914, **38**, 8. A. Clausen, D. R. P. 274345; abst. C. A. 1914, **8**, 3101; Chem. Zentr. 1914, **85**, 1, 2077; Wag. Jahr. 1914, **60**, 1, 292. Swiss P. 68190, 1914. J. Pintzsch Akt. Ges., E. P. 5026, 1912; abst. C. A. 1913, **7**, 2724; J. S. C. I. 1913, **32**, 691.
9. V. Höllding and H. Ditz, D. R. P. 142111, 1902; abst. Zts. ang. Chem. 1903, **16**, 583; Chem. Centr. 1903, **74**, 11, 76; Jahr. Chem. 1903, **56**, 345; Chem. Ztg. 1903, **27**, 599; Wag. Jahr. 1903, **49**, 1, 260; Mon. Sci. 1904, **61**, 6; 1905, **63**, 135; Chem. Zts. 1904, **3**, 13, 276, 501; J. S. C. I. 1903, **22**, 794. F. P. 326321, 1902. E. P. 21256, 1902; abst. J. S. C. I. 1903, 796, 1243. Farb. vorm. F. Bayer & Co., F. P. 460074, 1913. See C. Böhm, Chem. Ind. 1913, 120.
10. H. v. Keler and A. Weindel, U. S. P. 1102670, 1914. F. P. 460074, abst. J. S. C. I. 1914, **33**, 32, 831. Can. P. 190755, 1919; abst. C. A. 1919, **13**, 1747.
11. J. Dewar and A. Liebmann, E. P. 12981, 1913; abst. C. A. 1914, **8**, 3843; J. S. C. I. 1914, **33**, 797. Badisch: Anilin u. Sodafabrik, E. P. 6828, 1901; abst. J. S. C. I. 1902, **21**, 344; J. Soc. Dyers Col. 1902, **18**, 114.
12. H. Hilbert, F. P. 389032, 1908; abst. Mon. Sci. 1909, **71**, 111.
13. A. Gernot and H. Fievet, U. S. P. 697138, 1902; E. P. 2407, 1901; abst. J. S. C. I. 1902, **21**, 176, 1139. See also Terrisse, Bull. Soc. Ind. Mulhouse, 1902, 209; abst. J. S. C. I. 1903, **22**, 553. H. Hutchinsdn, E. P. 2843, 1883, abst. Wag. Jahr. 1884, **30**, 1238.

air or oxygen has been described by I. Kitsee,¹ E. Riesenfeld,² H. Kühne,³ and F. Cottrell.⁴ The Carborundum Co. of Niagara Falls proposes an electrically heated contact mass,⁵ while the electrolytic oxidation of sulfurous acid in solution has been described.⁶

Absorption of Sulfur Trioxide. The difficulty of absorbing sulfur trioxide in water or dilute sulfuric acid has already been touched upon. In this connection it must be remembered that a considerable amount of sulfuric acid is used in many contact processes for drying gases, and in the Badische process dilute acid is also produced by scrubbing the burner gases in the purification process, and this weak acid must again be brought up to strength. In the Badische process 6% to 8% of the total sulfur oxides are removed in the washing, and as the gases after this process are moist, a considerable amount of sulfur trioxide (up to 60%), are removed as H_2SO_4 in the drying.

In the Badische process of absorption, three towers containing sulfuric acid are used. The first contains 98% H_2SO_4 , which is enriched to oleum containing 25% free SO_3 , which passes to the second tower in which it is brought up to 60% free SO_3 . The third tower contained 60% H_2SO_4 , which is concentrated to 98% acid for the first tower. According to Knietsch, acid of strength less than 97%–98% H_2SO_4 should not be used in the first tower, otherwise loss as fume will occur. These towers are constructed of iron, wrought iron standing the action of the fuming acid containing more than 27% free SO_3 . The absorbers containing acids with less SO_3 , are constructed of cast-iron. The gases are passed into the acid through serrated iron hoods.

The temperature of absorption should be between 95° and

1. U. S. P. 869094, 1907; abst. Mon. Sci. 1908, **69**, 50.
2. D. R. P. 229274, 1909; abst. J. S. C. I. 1911, **30**, 129; C. A. 1911, **5**, 2314; Zts. ang. Chem. 1911, **24**, 88; Chem. Zentr. 1911, **82**, I, 178; Chem. Ztg. Rep. 1911, **35**, 3; Wag. Jahr. 1911, **57**, I, 422.
3. E. P. 17520, 1908; abst. J. S. C. I. 1909, **28**, 982. Belg. P. 210029, 1908.
4. E. P. 21147, 1907; abst. J. S. C. I. 1908, **27**, 404.
5. C. Brockbank, assignor to The Carborundum Co., U. S. P. 1157293, 1914; abst. J. S. C. I. 1915, **34**, 1197.
6. C. Jacobs, U. S. P. 704831, 1902; abst. J. S. C. I. 1902, **21**, 1077; J. A. C. S. 1903, **25R**, 100; Mon. Sci. 1902, **58**, 184. B. Bradley, E. P. 16152, 1911; abst. J. S. C. I. 1911, **30**, 930.

115° F,¹ and preferably at or near the latter temperature.

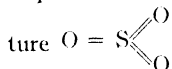
The acidity of the effluent from contact plants has been examined,² the estimation of acidity following the usual lines.

H. Weber³ absorbs sulfur trioxide in cooled and stirred 100% sulfuric acid until at least 5% of the anhydride is absorbed, and then adds dilute sulfuric acid until the strength is reduced to 98%. By proceeding in this manner, the difficulties of absorbing sulfur trioxide in weak acid are avoided and iron vessels may be used.

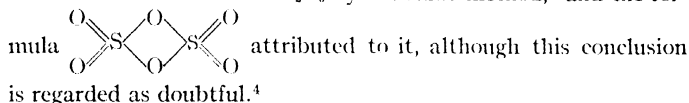
Properties of Sulfur Trioxide. SO₃ contains 40.05% by weight of sulfur and 59.95% of oxygen, its molecular weight being 80.06. According to H. Giran⁴ the density of the vapor at the moment of formation corresponds with the simple formula. Earlier experimenters⁵ noticed that the substance may exist in two modifications, called liquid sulfur trioxide, or α -SO₃, and solid sulfur trioxide, or β -SO₃. The former is the first product of the contact process, and results when sulfuric acid is distilled with phosphorus pentoxide, or when fuming sulfuric acid is distilled. The solid form is produced from the liquid upon keeping for some time, particularly in presence of traces of moisture. Liquid sulfur trioxide purified by repeated distillation over phosphorus pentoxide, is a colorless fluid,⁶ which on cooling solidifies to long colorless needles, of sp. gr. 1.9457 at 11.8°, m. pt. 16.79°. The specific

1. I. Cox, E. P. 8528, 1911; abst. C. A. 1912, **6**, 2825; J. S. C. I. 1912, **31**, 187. U. S. P. 1002824; abst. C. A. 1911, **5**, 3911; Chem. Ztg. Rep. 1911, **35**, 545. G. Stone, U. S. P. 695180; abst. J. S. C. I. 1902, **21**, 476. J. Herreshoff, U. S. P. 722981, 1903. Schlamp vom Hofe & Co., D. R. P. 166599. Deutsche Ton und Steinzeug Akt. Ges. recommend the use of Cellarius receivers. F. Cottrell, E. P. 21147, 1907; U. S. P. 866843, 866844; E. P. 382179; D. R. P. 208740. I. Cox, E. P. 8528, 1911; U. S. P. 1002824, 1911; abst. J. S. C. I. 1911, **30**, 1210; 1912, **31**, 187.
2. British Alkali Inspectors Reports: No. 38, 16; No. 40, 28, 121, 160, 179; No. 41 (1904), 18, 92, 93, 132, 147, 151; No. 42 (1905), 153, 156. See also H. Ljungh, Chem. Ztg. 1909, **33**, 143; abst. Chem. Zentr. 1909, **80**, I, 1201; C. A. 1909, **3**, 1327.
3. U. S. P. 1291306, 1919; abst. J. S. C. I. 1919, **38**, 499-A; C. A. 1919, **13**, 892; Chim. Ind. 1920, **3**, 207. Compare British Dyes Ltd., J. Turner and W. Davidson, E. P. 132923, 1918; abst. C. A. 1920, **14**, 316. See also E. P. 131512, 132387, 132661, 1918; abst. C. A. 1920, **14**, 324.
4. Compt. rend. 1913, **157**, 375; abst. C. A. 1913, **7**, 3933; Chem. Zentr. 1913, **74**, II, 1196.
5. C. Marignac, Arch. Sci. Phys. Nat. 1853, **22**, 225; 1875, **52**, 236; 1877, **58**, 228. C. Schultz-Sellack, Ber. 1870, **3**, 215. H. Buff, Ann. 1865-1866, Suppl. **4**, 151.
6. R. Weber, Pogg. Ann. 1876, **159**, 313; Ber. 1886, **19**, 3187. D. Lichty, J. A. C. S. 1912, **34**, 1440; abst. C. A. 1912, **6**, 2880; 1913, **7**, 14.

gravity of the liquid at 48° is 1.7921. Coefficient of expansion of the solid at 11.5° is 0.000676, and of the liquid at 48°, 0.002805. This expansion is regular between 11° and 45°, although R. Schenck¹ asserts that a contraction occurs at 35°. The boiling points at 740.7 mm. and 744.5 mm. are 44.23° and 44.36° respectively, corresponding with a boiling point of 44.88° at 760 mm. The molecular weight of the liquid modification in solution corresponds with the formula SO_3 ,² and this probably has the structure



The molecular weight of the solid modification has been found to be S_2O_6 by the same method,³ and the formula



The solid modification is an asbestos-like crystalline solid, of specific gravity 1.97 at 20°.⁵ It sublimates at 50°, the product of distillation being the liquid form.

The heat of formation of 1 mol. SO_3 (80.06 gm.) is 103.230 kgm. cal. from S and 3O; from SO_2 and O it is 34.4 kgm. cal. in the solid state or 22.6 kgm. cal. in the gaseous state. J. Partington⁶ finds the value 22.27 kgm. cal. agrees better with the equilibrium results than Berthelot's value of 22.6. The latent heat of evaporation of 1 mol. of SO_3 is 11.8 kgm. cal., and the heat of solution in a large quantity of water, 39.17 kgm. cal.

In moist air, sulfur trioxide forms dense white fumes of sulfuric acid, and when thrown into water it hisses; organic matter is charred, and the skin rapidly attacked. In the complete absence of moisture it does not redden litmus paper, but dissolves sulfur, forming a blue solution, from which green crystals of sul-

1. Ann. 1901, **316**, 1; abst. J. C. S. 1901, **80**, ii, 380; J. S. C. I. 1901, **20**, 577.

2. G. Oddo, Rend. Acc. Lincei, 1901, (5), **10**, 207; abst. Chem. Centr. 1901, **72**, II, 969. Gazz. chim. ital. 1901, **31**, II, 158.

3. G. Oddo, Rend. Acc. Lincei, 1901, (5), **10**, 207; abst. Chem. Centr. 1902, **72**, II, 969. Gazz. chim. ital. 1901, **31**, II, 158.

4. R. Weber, Pogg. Ann. 1876, **159**, 313; Ber. 1886, **19**, 3187. D. Lichty, J. A. C. S. 1912, **34**, 1440; abst. C. A. 1912, **6**, 2880; 1913, **7**, 14.

5. C. Marignac, Arch. Sci. Phys. Nat. 1853, **22**, 225; 1875, **52**, 236; 1877, **58**, 228. C. Schultz-Sellack, Ber. 1870, **3**, 215. H. Buff, Ann. 1865-1866, Suppl. **4**, 151.

6. "The Alkali Industry," 1918, 43.

fur sesquioxide, S_2O_3 , separate.¹ Selenium and tellurium are also dissolved, producing green and red solutions respectively, which probably contain the oxides $SSeO_3$ and $STeO_3$.²

Sulfur trioxide on passing through a red-hot tube decomposes into sulfur dioxide and oxygen, but is re-formed from these gases at lower temperatures in presence of catalysts, the reaction being reversible.³

It combines with iodine to form the stable compounds $I_2(SO_3)_6$ and $I_2(SO_3)_2$, and with many salts.⁴

Analysis of Oleum. The sample is taken by means of a long glass tube, about half an inch in diameter drawn out to about $1/4$ in. at the lower end, and transferred to a dry and wide-mouth, stoppered bottle. Before sampling, the container should be agitated in order to mix the contents. Tanks are sampled in a similar manner, or a sample is received in a lead jug during discharging. The bottle, of course, is kept closely stoppered between each sampling.

In the laboratory, the bottle is thoroughly shaken, and the following tests made:

(1) *Specific gravity* is determined by the hydrometer, and corrected by a table to 15.5° , or by a 25 cc. pycnometer under standard conditions.

(2) *Total Acidity.* About 2 gm. is weighed out in an oleum bulb consisting of a thin glass bulb with two capillary arms supported in a small crucible for weighing, and a sample of acid introduced by suction with a filter pump. The capillary arms are wiped with filter or tissue paper, and the bulb re-weighed. The bulb is then dropped into a wide-mouth bottle containing 100 cc. distilled water, and the bottle immediately stoppered. Sufficient time is allowed for the fumes to subside, the bottle is shaken, the bulb being first broken by a glass rod, the stopper and rod are rinsed into the bottle, and the acid titrated with normal soda, using methyl orange as indicator, the percentage of total acid

1. R. Weber, Pogg. Ann. 1875, **156**, 531; abst. Jahr. Chem. 1875, **28**, 158.

2. E. Moles, Ann. Fis. Quim. 1915, **13**, 134; J. Chim. Phys. 1915, **13**, 207; abst. J. S. C. I. 1915, **34**, 960.

3. M. Bodenstein and F. Kranendieck, Zts. physik. Chem. 1912, **80**, 148; abst. Chem. Zentr. 1912, **83**, 11, 1092. See W. Beatty, Belg. P. 252593, 1913.

4. W. Traube, Ber. 1913, **46**, 2513; abst. J. S. C. I. 1913, **32**, 1008.

obtained in the titration, being calculated as sulfur trioxide.

•(3) *Free Sulfur Trioxide.* This is obtained from the percentage of total SO_3 by the formula:

$$\text{Free SO}_3 \text{ per cent.} = \frac{(\text{Total H}_2\text{SO}_4 \text{ per cent.} - 100) 0.22505}{1}$$

(4) *Arsenic.* The percentage of arsenic in oleum is determined by the Gutzeit test. About 2 cc. of the sample are accurately measured out and diluted to 50 cc. with distilled water in a graduated flask. One cc. is then pipetted into a test-tube and 5 cc. of distilled water and 1 gm. arsenic-free zinc added. A plug of lead acetate wool is inserted in the mouth of the tube, and a piece of mercuric chloride paper folded over the top and held in place by a rubber band. The tube is slightly warmed to start the reaction, and then allowed to stand at room temperature for 30 minutes. The stain on the mercuric chloride paper is then compared with a set of standard stains prepared with known amounts of arsenic.

Plant Tests. A test of the SO_3 content of oleum at the plant may be carried out by mixing the oleum with the feed acid to the absorbers, and noting the rise in temperature. The test may be made on the feed acid, if this is poured into oleum.

A. For Oleum. Measure 200 cc. of feed acid (92.5% to 94.5% H_2SO_4) into a porcelain dish, and determine the temperature (b°). Measure out 200 cc. of oleum and do likewise (a°). Pour the oleum quickly into the acid, stirring vigorously, and note the maximum temperature (c°). The rise of temperature is $c - (a + b)/2$. The percentage SO_3 in the oleum is found from Table LIX.

B. For Feed-Acid 96% to 100%. Proceed as in A, but pour the acid into 20%–25% oleum. Rise = $c - (a + b)/2$. Refer to Table LIX.

C. Feed-Acid 88% to 96%. Measure 300 cc. oleum into a dish and observe the temperature (a°). Measure out 100 cc. of the sample of acid, and take the temperature (b°). Pour the acid into the oleum, stirring vigorously. Maximum temperature is c° . Rise of temperature is $c - (3a + b)/4$. Refer to Table LXI.

Acidity Tests in the Exit Gases of Oleum Plant. The total acidity, SO_2 and SO_3 is determined, no differentiation being made. A continuous test is run during the night, the determination being

usually made in the laboratory the following day.

A Buchner flask is fitted with a $\frac{1}{2}$ -in. stout wall glass tube, closed at the bottom, but has a few holes blown in it, and packed with glass beads. The holes, at the lower extremity, dip under 25 cc. *N*/NaOH diluted with water, and is connected with an aspirator, so that gas is drawn up the inner tube. The liquid is titrated with *N* acid and phenolphthalein, and the acidity calculated in gm. SO_3 per cu. ft.

Moisture Test on Grillo Plant. This test is made on the cooled purified gases passing to the converters. A large volume of gas is aspirated through U-tubes packed with phosphorus pentoxide, the moisture and acid mist being weighed together, and expressed in grams per 100 liters. About 40 to 50 liters are aspirated, and three U-tubes are used, two being packed with P_2O_5 and glass wool which are weighed, and one filled with calcium chloride as a guard tube before the aspirator.

| TABLE LXIX | | | | TABLE LX | | TABLE LXI | | | |
|------------|---------------------------------|------|---------------------------------|----------|---|-----------|---|------|---|
| Rise | $\frac{C}{\%}$ SO_2 | Rise | $\frac{C}{\%}$ SO_3 | Rise | $\frac{C}{\%}$ H_2SO_4 | Rise | $\frac{C}{\%}$ H_2SO_4 | Rise | $\frac{C}{\%}$ H_2SO_4 |
| 1 | 0.5 | 21 | 12.1 | | | 6 | 98.8 | 26 | 92.6 |
| 2 | 1.1 | 22 | 12.8 | | | 7 | 98.5 | 27 | 92.3 |
| 3 | 1.6 | 23 | 13.4 | 2 | 99.9 | 8 | 98.1 | 28 | 92.1 |
| 4 | 2.2 | 24 | 14.1 | 4 | 99.5 | 9 | 97.7 | 29 | 91.8 |
| 5 | 2.7 | 25 | 14.7 | 6 | 99.3 | 10 | 97.4 | 30 | 91.6 |
| 6 | 3.3 | 26 | 15.4 | 8 | 99.0 | 11 | 97.1 | 31 | 91.3 |
| 7 | 3.8 | 27 | 16.0 | 10 | 98.7 | 12 | 96.7 | 32 | 91.0 |
| 8 | 4.4 | 28 | 16.7 | 12 | 98.4 | 13 | 96.4 | 33 | 90.8 |
| 9 | 4.9 | 29 | 17.4 | 14 | 98.1 | 14 | 96.1 | 34 | 90.6 |
| 10 | 5.5 | 30 | 18.0 | 16 | 97.8 | 15 | 95.7 | 35 | 90.3 |
| 11 | 6.1 | 31 | 18.7 | 18 | 97.5 | 16 | 95.5 | 36 | 90.1 |
| 12 | 6.7 | 32 | 19.4 | 20 | 97.3 | 17 | 95.1 | 37 | 89.8 |
| 13 | 7.3 | 33 | 20.1 | 22 | 96.9 | 18 | 94.9 | 38 | 89.6 |
| 14 | 7.9 | 34 | 20.8 | 24 | 96.7 | 19 | 94.6 | 39 | 89.4 |
| 15 | 8.5 | 35 | 21.5 | 26 | 96.4 | 20 | 94.3 | 40 | 89.1 |
| 16 | 9.1 | 36 | 22.2 | 28 | 96.1 | 21 | 94.0 | 41 | 88.9 |
| 17 | 9.7 | 37 | 22.9 | 30 | 95.8 | 22 | 93.7 | 42 | 88.7 |
| 18 | 10.3 | 38 | 23.6 | | | 23 | 93.4 | 43 | 88.5 |
| 19 | 10.9 | 39 | 24.3 | | | 24 | 93.1 | 44 | 88.2 |
| 20 | 11.5 | 40 | 25.0 | | | 25 | 92.9 | 45 | 87.9 |

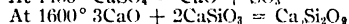
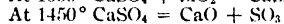
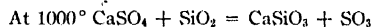
Manufacture of Oleum from Sulfates. One of the most promising sulfates for the manufacture of oleum is calcium sulfate,

which occurs in large quantities as the mineral anhydrite, CaSO_4 , and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This would furnish a cheap source of acid if the latter could be produced from it. Although numerous attempts have been made to effect this, the process does not appear to have been commercially successful. A recent proposal of the Badische Co. to utilize gypsum as the source of sulfuric acid in making ammonium sulfate from synthetic ammonia, seems more promising.

A. Bambach¹ decomposes gypsum in a current of air in a furnace at a high temperature, which is similar to the process described by M. Prud'homme,² who proposes to add silica, alumina, or oxide of iron if necessary. E. Natho³ heats a mixture of equivalent amounts of calcium sulfate and silica with a little water in an autoclave, and claims that the reaction is complete at 600° . N. Basset⁴ combines a mixture of gypsum and tar into balls, heats these to form calcium sulfide, and decomposes this with carbon dioxide as in the Chance process. L. Basset⁵ heats a mixture of clay and a material containing calcium sulfate to produce cement and gases containing sulfur dioxide. The latter, mixed with air, is to be passed over a catalyst to form sulfur trioxide. The Elektrizitätswerk Lonza⁶ heats gypsum and quartz in an atmosphere enriched in oxygen to prevent dissociation of SO_3 into SO_2 and O_2 . H. Hilbert⁷ proposes to use calcium and barium sulfates instead of lime or calcium carbonate in the manufacture of glass, and to condense the sulfur trioxide produced in the fusion process. About 1400° is stated to be a suitable temperature to employ. P. Cantilena⁸ burns finely powdered gypsum and clay, mixed in the ratio of 0.43 to 0.5, molded with water into small bricks, to 1600° in a plentiful supply of air. The following

1. Ital. P. 139955, 1914; abst. C. A. 1915, **9**, 2804.
2. F. P. 400030, 1908; abst. C. A. 1911, **5**, 574; Chem. Ztg. Rep. 1909, **33**, 445; Mon. Sci. 1910, **73**, 164.
3. D. R. P. 265835; abst. C. A. 1914, **8**, 409; Zts. ang. Chem. 1913, **26**, 675; Chem. Zentr. 1913, **84**, II, 1630; Chem. Ztg. Rep. 1913, **37**, 600; Wag. Jahr. 1913, **59**, I, 382.
4. F. P. 331897, 1903; abst. J. S. C. I. 1903, **22**, 1194.
5. E. P. 100597, 1916; abst. J. S. C. I. 1917, **36**, 138. Can. P. 192662, 1920. U. S. P. 1197331, 1916; abst. J. S. C. I. 1916, **35**, 1058; Ann. Rep. Chem. Soc. Ind. 1917, **2**, 181; Mon. Sci. 1917, **84**, 49.
6. Swiss P. 72627, 1916; abst. C. A. 1916, **10**, 2391.
7. F. P. 389032, 1908; abst. J. S. C. I. 1908, **27**, 939; Mon. Sci. 1909, **71**, 111.
8. Ind. Chim. **14**, 39; abst. C. A. 1914, **8**, 1331.

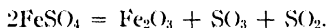
series of chemical reactions are said to occur as below indicated:



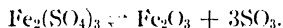
At these temperatures, however, all the sulfur trioxide would be dissociated.

The original method for the manufacture of oleum before the introduction of the contact processes, involved the decomposition of certain sulfates by heating them to a high temperature, sulfur trioxide being evolved.

The process of distilling ferrous or ferric sulfates began near Pilsen in the sixteenth century and spread to Saxony and the Hartz. It was worked in Bohemia from 1790 to 1900,¹ when it was abandoned on account of the introduction of the contact processes. The substance first used was green vitriol, dried so as to remove as much water of crystallization as possible, and then heated to redness in fireclay retorts.



Later on crude ferric sulfate, prepared by the weathering and lixiviation of shales containing pyrites was used.



Since fuming acid was made, the ferric sulfate was often produced by treating ferric oxide with strong sulfuric acid, heating till the water is driven off, and then distilling at a higher temperature, the residue of ferric oxide being then re-used. In other cases, pyrosulfates, such as $\text{Na}_2\text{S}_2\text{O}_7$, prepared by the heating of acid sulfates such as NaHSO_4 .²

The only normal sulfate which is suitable for the process is ferric sulfate. In the case of other sulfates, such as those of zinc, copper, aluminium and magnesium, decomposition takes place only at such a high temperature that the sulfur trioxide is changed into SO_2 and oxygen. The decomposition of ferric sulfate takes

1. E. Jahn, *Wag. Jahr.* 1873, **19**, 220. F. Stolba, *Wag. Jahr.* 1885, **31**, 316.
2. J. Wolters, D. R. P. 12295, 15639; abst. *Wag. Jahr.* 1881, **27**, 166. E. P. 263, 1880. U. S. P. 223571, 1880; abst. J. A. C. S. 1880, **2**, 67. H. Baum, D. R. P. 40696; *Wag. Jahr.* 1887, **33**, 528. R. Wallace, E. P. 2285, 1876. P. Prelier, E. P. 11773, 1847. See also H. Schulze, *Ber.* 1884, **17**, 2705. For the suggested manufacture of fuming sulfuric acid from bisulfates and boric acid, see Karl-Stohmann, *Chemie*, 3d ed. **6**, 156. See J. S. C. I. 1918, **37**, 263-R.

place at a dark red heat, and the sulfur trioxide is largely given off unchanged. The reaction has been investigated by G. Lunge and G. Pollitt, G. Keppeler, G. Lunge and K. Reinhardt, and F. Küster.

Decomposition in a partial vacuum has been applied by R. Schuberth,¹ who describes a special apparatus for carrying out the process. The use of aluminium sulfate,² magnesium sulfate,³ and zinc sulfate,⁴ have also been proposed.

Production of Oleum Other than by the Contact Process. A description has already been given of the old method of producing oleum by distilling sulfates. In addition, a number of other processes have been proposed which do not involve catalysts, but none of them appear to have been used, at least not extensively.

A. Nobel and G. Felirenbach⁵ pass the vapor of boiling sulfuric acid over lumps of metaphosphoric acid heated to 320°, which retains water and some sulfuric acid, while sulfur trioxide vapor is evolved. R. Frank⁶ burns sulfur in oxygen under at least 100 atm. pressure, which is said to lead to a quantitative production of sulfur trioxide. The latter is collected by the cooling of the gas by rapid expansion, when the trioxide crystallizes out. O. Bender⁷ burns a mixture of sulfur dioxide and oxygen, with or without nitrogen, in an oxy-hydrogen flame. Sulfur trioxide is formed from the dioxide with evolution of heat, and is therefore favored by as low a temperature as possible.

O. Niedenführ⁸ distills oleum continuously by the waste heat

1. D. R. P. 52000, 1889; abst. Zts. ang. Chem. 1890, **3**, 368; Wag. Jahr. 1890, **36**, 467; Ber. 1890, **23**, 515.

2. H. Blackmore, U. S. P. 724251, 1903, abst. J. S. C. I. 1903, **22**, 554; Chem. Ztg. 1903, **27**, 393; Mon. Sci. 1903, **59**, 170; Chem. Zts. 1903, **2**, 544; J. A. C. S. 1903, **25R**, 497. Cf. Gorman, E. P. 919, 1879.

3. E. Sonstadt, E. P. 1638, 1875. See also D. R. P. 6091, 1878; abst. J. A. C. S. 1879, **1**, 404. J. Wolters, D. R. P. 3110, 1878; abst. Chem. Ind. 1878, **1**, 329.

4. J. Cullen, U. S. P. 1278308; abst. C. A. 1918, **12**, 2414; J. S. C. I. 1918, **37**, 766-A; Mon. Sci. 1919, **86**, 26.

5. E. P. 10860, 1884. U. S. P. 310147, 1884; abst. J. S. C. I. 1885, **4**, 498. See also H. Angerstein, D. R. P. 26959, 1883; abst. J. S. C. I. 1884, **3**, 481.

6. D. R. P. 194879, 1906; abst. Chem. Ztg. 1908, **32**, 128, 219; J. S. C. I. 1908, **27**, 400, 502; Zts. ang. Chem. 1908, **21**, 796; Chem. Zentr. 1908 **79**, I, 909; Jahr. Chem. 1905-1908, I, 1625; Chem. Zts. 1908, **7**, 756; Wag. Jahr. 1908, **54**, I, 373.

7. D. R. P. 195810; abst. Zts. ang. Chem. 1908, **21**, 1371; Chem. Zentr. 1908, **79**, I, 1218; Jahr. Chem. 1905-1908, I, 1612; Chem. Ztg. Rep. 1908, **32**, 228; Chem. Zts. 1908, **7**, 755.

8. D. R. P. 230533; abst. C. A. 1911, **5**, 2707; Zts. ang. Chem. 1911,

of pyrites burner gases to produce sulfur trioxide. G. Léon¹ electrolyzes sulfuric acid of 66° or 65.5° Bé. in a cast-iron tank, cooled externally and covered with a slate slab. In the center is a hollow platinum anode, water cooled, and this is surrounded by an open annular cathode. It is stated that 1 kgm. sulfur trioxide can be produced by an expenditure of 0.9 h. p. hour. W. Garroway² and F. Riesenfeld³ submit gases containing sulfur dioxide and oxygen to the action of electrical discharges. Exposure to ultraviolet light has been proposed by A. Coehn and H. Becker,⁴ who use a special lamp working with a low pressure of mercury vapor. D. Berthelot and H. Gaudechon⁵ find that sulfur dioxide is decomposed by ultraviolet light, with formation of sulfur trioxide and sulfur. This action, under the influence of ordinary light was noticed many years ago by Tyndall.

O. von Gruber⁶ heats chamber crystals, or nitrosulfonic acid, with dry air and sulfur dioxide to produce sulfur trioxide, the nitrogen oxides being recovered.

The absorption of sulfur trioxide from kiln gases has been proposed. W. Majers and R. Messel⁷ carry out the absorption in concentrated sulfuric acid. I. Cox,⁸ for the du Pont Powder Co., maintains the gases and acid at the optimum temperature 29.4°–46°, and regulates the proportion between the absorbing acid and the gases so that the ratio of the acid to the sulfur trioxide is never below 43 to 1. T. Briggs and H. Merriam⁹ bring

24, 376; Chem. Zentr. 1911, **82**, I, 521; Chem. Ztg. Rep. 1911, **35**, 78; Wag. Jahr. 1911, **57**, I, 422; Mon. Sci. 1914, **81**, 84.

1. F. P. 206088, 1890. D. R. P. 57118; abst. Wag. Jahr. 1891, **37**, 342; Zts. ang. Chem. 1891, **4**, 464; Ber. 1892, **25**, 51; Mon. Sci. 1891, **38**, 223.

2. F. P. 1755, 1903; abst. J. S. C. I. 1904, **23**, 252.

3. D. R. P. 229274; abst. C. A. 1911, **5**, 2314; Zts. ang. Chem. 1911, **24**, 88; Chem. Zentr. 1911, **82**, I, 178; Chem. Ztg. Rep. 1911, **35**, 3; Wag. Jahr. 1911, **57**, I, 422.

4. D. R. P. 217722; abst. Zts. ang. Chem. 1910, **23**, 764; Chem. Zentr. 1910, **81**, I, 585; Jahr. Chem. 1910, **63**, I, 526; Chem. Ztg. Rep. 1910, **34**, 50; Wag. Jahr. 1910, **56**, I, 419; Mon. Sci. 1913, **79**, 158; Chem. Zts. 1910, **9**, 1774.

5. Compt. rend. 1910, **150**, 1517; abst. Chem. Zentr. 1910, **81**, II, 365; C. A. 1910, **4**, 2612; J. C. S. 1910, **98**, ii, 606.

6. D. R. P. 277726; abst. Wag. Jahr. 1884, **30**, 300; Ber. 1884, **17**, R-337.

7. F. P. 1201, 1878; abst. Wag. Jahr. 1879, **25**, 287; J. A. C. S. 1879, **1**, 296. Ber. 1879, **12**, 860; Chem. Ind. 1879, **2**, 158; Dingl. Poly. 1879, **233**, 143.

8. U. S. P. 1002824. E. P. 8528, 1911; abst. C. A. 1911, **5**, 3911; 1912, **6**, 2825; J. S. C. I. 1912, **31**, 187; Chem. Ztg. Rep. 1911, **35**, 545.

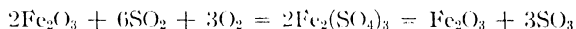
9. U. S. P. 1013638; abst. C. A. 1912, **6**, 671; Chem. Ztg. Rep. 1912, **36**, 194; Mon. Sci. 1912, **77**, 130. See also G. Evans, E. P. 11338, 1907;

sulfur trioxide and air in contact with a spray of sulfuric acid (94% to 95.5%) moving in the opposite direction, the apparatus being cooled externally.

According to W. Seaman¹ sulfur trioxide is produced by fusing a mixture of sodium sulfate, calcium sulfate and silica, in the absence of a reducing environment to avoid excessive decomposition of the sulfur trioxide formed.

P. Schulze-Berge² recovers sulfur trioxide from the manufacture of dyestuffs by distillation at a low temperature in a vacuum.

Theory of the Contact Process. Reference has already been made to the general theory of catalytic processes, with special reference to the contact process. The rôle of iron oxide seems to be fairly well established as an intermediate-compound action, ferric sulfate being alternately produced and decomposed:



Thus the sulfur trioxide is produced by the decomposition of a compound which can be formed under the same conditions from sulfur dioxide and oxygen.³

The action of platinum is not so clear, but it may be assumed that an intermediate oxide of platinum is produced, and decomposed by the sulfur dioxide, oxidizing this to sulfur trioxide and becoming reduced again to platinum.⁴

The problems of the equilibrium conditions and of the •

abst. J. S. C. I. 1908, **27**, 684. J. Black and M. M. Chappell, U. S. P. 1031413, 1912. V. Defays, Belg. P. 201102, 1907. E. Kendall, U. S. P. 323583, 1885; abst. Wag. Jahr. 1885, **31**, 220.

1. U. S. P. 1292098; abst. C. A. 1919, **13**, 998; J. S. C. I. 1919, **38**, 286 A; Mon. Sci. 1919, **86**, 49; Chim. Ind. 1920, **3**, 207.

2. D. R. P. 35620; abst. Wag. Jahr. 1886, **32**, 404.

3. G. Keppeler, Zts. ang. Chem. 1908, **21**, 532, 577; abst. J. S. C. I. 1908, **27**, 402; See also J. S. C. I. 1902, **21**, 1137. G. Lunge, Zts. ang. Chem. 1902, **15**, 149. G. Lunge and G. Pollitt, J. S. C. I. 1903, **22**, 79. G. Lunge and K. Reinhardt, Zts. ang. Chem. 1904, **17**, 1041. E. Berl, Zts. ang. Chem. 1905, **18**, 254; Zts. anorg. Chem. 1905, **44**, 267. L. and P. Wöhler and W. Plüddemann, Zts. physik. Chem. 1908, **62**, 641. J. d'Ans, Dissertation, Kiel, 1905; abst. Zts. physik. Chem. 1908, **62**, 89; Zts. ang. Chem. 1908, **21**, 532, 577.

4. C. Engler and L. Wöhler, Zts. anorg. Chem. 1902, **29**, 1. See also F. Haber and S. Grinberg, Zts. anorg. Chem. 1898, **18**, 39; Zts. physik. Chem. 1900, **34**, 515. G. Bredig, Zts. physik. Chem. 1899, **31**, 294, 346; Anorg. Fern. 1901, 942. L. Mond, W. Ramsay and J. Shields, Zts. physik. Chem. 1898, **25**, 685. J. Brode, Zts. physik. Chem. 1901, **37**, 257. H. Wieland, Ber. 1912, **45**, 685. G. Keppeler, Zts. ang. Chem. 1902, **15**, 809. J. Conroy, J. S. C. I. 1902, **21**, 302. E. Russell and N. Smith, J. C. S. 1900, **77**, 340.

kinetics of the contact process have been studied by numerous investigators, with the result that, in the first case, the law of mass-action has been confirmed.

The catalytic action of platinum in the formation of sulfur trioxide: $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ is technically feasible between 400° and 500° . At lower temperatures the reaction is too slow to be of any service, but, since it is exothermic, the reverse reaction sets in even at 400° , and the conversion cannot be complete under any conditions of working. This conclusion from the law of mass-action has been completely confirmed. The reverse reaction: $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$ is practically complete at 1000° . Although an increase of temperature favors the speed of the reaction, it diminishes the equilibrium yield, and an optimum condition of temperature has to be selected. This has been found by experiment to be about 450° in the case of platinum, and in technical working this temperature should be aimed at.

A large number of experiments have been described by Knietsch in his original memoir on the contact process,¹ and sets of curves are given for the equilibrium and velocity conditions. From the point of view of physical chemistry, however, Knietsch's results leave much to be desired, and fortunately we have in this field other more reliable data. Of these, the following tables, due to M. Bodenstein and W. Pohl² may serve to indicate the equilibrium conversions under various conditions.

In these results we notice one or two facts of importance. In the first place it is evident that the conversion in the equilibrium state is high. With pure oxygen, as is seen from Table LXIII, the equilibrium conversion is very nearly 100%. In this respect the contact process differs from some other catalytic processes, such as the Deacon process for the manufacture of chlorine, where the equilibrium conversion is of the order of 66%

1. R. Knietsch, Ber. 1901, **34**, 4093. See also S. Geary, J. S. C. I. 1919, **38**, 133-T. R. Curtis, J. S. C. I. 1919, **38**, 196-T.

2. See also O. Sackur, Zts. Elektrochem. 1901-1902, **8**, 47. M. Bodenstein and C. Fink, Zts. physik. Chem. 1907, **60**, 1. R. Lucas, Zts. Elektrochem. 1905, 457. L. Wöhler, A. For's and W. Plüddemann, Ber. 1906, **39**, 3538. L. Wöhler, Zts. Elektrochem. 1905, **12**, 844. G. Bodländer and K. Köppen, Zts. Elektrochem. 1903, **9**, 559, 698, 787. Fifth Intl. Cong. Appl. Chem. 1904, **4**, 624. F. Küster, Zts. anorg. Chem. 1904, **42**, 453. J. Brode, Zts. ang. Chem. 1902, **15**, 1081. R. Knietsch, Fifth Intl. Cong. Appl. Chem. 1904, **1**, 614. M. Bodenstein, Chem. Ztg. 1902, **26**, 1077. W. Caspari, Chem. Trade J. 1914, **54**, 336. M. Bodenstein and C. Fink, Zts. physik. Chem. 1907, **60**, 1; abst. J. S. C. I. 1908, **27**, 120.

TABLE LXII.—CONVERSION OF A MIXTURE OF SO_2 AND O_2 IN THE THEORETICAL PROPORTIONS ($2\text{SO}_2 + \text{O}_2$) AT VARIOUS TEMPERATURES WHEN DILUTED WITH NITROGEN

| No. | Amount of N_2 Added | SO_2 | O_2 | 400° | 500° | 600° | 700° | 800° | 900° |
|-----|------------------------------|---------------|--------------|------|------|------|------|------|------|
| I | | 66.67 | 33.33 | 98.1 | 91.3 | 76.3 | 71.5 | 30.1 | 16.0 |
| II | 79.00 | 14.00 | 7.00* | 96.3 | 84.7 | 62.2 | 35.2 | 18.3 | 8.2 |
| III | 84.85 | 10.10 | 5.05 | 95.7 | 83.2 | 59.1 | 31.9 | 15.0 | 7.0 |
| IV | 89.50 | 7.00 | 3.50 | 95.2 | 81.2 | 55.5 | 28.5 | 12.9 | 6.0 |
| V | 97.00 | 2.00 | 1.00 | 92.7 | 73.2 | 43.0 | 18.4 | 7.5 | 3.3 |

*Gas obtained by burning sulfur in air.

TABLE LXIII.—SULFUR DIOXIDE AND OXYGEN WITHOUT NITROGEN

| No. | SO_2 | O_2 | 400° | 500° | 600° | 700° | 800° | 900° |
|-----|---------------|--------------|------|------|------|------|------|------|
| I | 66.67 | 33.33 | 98.1 | 91.3 | 76.3 | 51.5 | 30.1 | 16.0 |
| II | 33.33 | 66.67 | 99.7 | 97.3 | 88.5 | 66.6 | 40.4 | 22.0 |
| III | 14.00 | 86.00 | 99.8 | 97.9 | 90.3 | 69.8 | 43.9 | 24.4 |
| IV | 7.00 | 93.00 | 99.8 | 98.1 | 90.5 | 70.7 | 41.9 | 25.3 |
| V | 2.00 | 98.00 | 99.8 | 98.2 | 90.8 | 71.2 | 45.5 | 25.6 |

TABLE LXIV.—BURNER GAS DILUTED WITH AIR

| No. | Air % | N_2 | SO_2 | O_2 | 400° | 500° | 600° | 700° | 800° | 900° |
|-----|-------|--------------|---------------|--------------|------|------|------|------|------|------|
| I | | 84.85 | 10.10 | 5.00 | 96.2 | 83.2 | 59.1 | 39.1 | 15.0 | 7.0 |
| II | 1.444 | 83.00 | 7.00 | 10.00 | 99.3 | 93.4 | 73.3 | 42.5 | 20.5 | 9.8 |
| III | 2.194 | 81.40 | 4.00 | 14.60 | 99.4 | 94.9 | 78.3 | 48.1 | 24.2 | 11.7 |
| IV | 3.944 | 80.00 | 2.00 | 18.00 | 99.5 | 95.6 | 80.5 | 51.3 | 26.3 | 12.9 |

under workable conditions. When dilute gases are used, as is the case in practice when burner gas largely diluted with nitrogen is employed, the conversion might be expected to drop considerably. This, as a glance at Table LXIV will show, is not the case. If an excess of oxygen is used, the increment of conversion due to the increased mass of the oxygen is sufficient to bring the yield well above 95%, even with burner gas diluted with air, at temperatures which are workable, i. e., at which the velocity of the conversion is sufficiently high to make the process a technical possibility. With excess of air, the conversion again approaches

100%, but in practice it is necessary to consider the yield in a given time with a known bulk of catalytic material, or the space-time yield, and this requires that too dilute gases shall not be used. The best mean is, according to Haber¹ a gas of the composition SO₂, 7% by volume, O₂, 7% by volume, and N₂, 82.6% by volume, at temperatures from 434° to 550°. It is for this mixture that J. Partington² has calculated the equilibrium constant:

$$K' = p_{\text{SO}_2} p_{\text{SO}_2} p_{\text{O}_2}$$

where the value of p is the partial pressure in the mixture, i. e., the total pressure divided by the relative number of molecules of the constituent in the mixture, for various temperatures. The results are given by the formula:

$$\log_{10} K' = \frac{4875}{T} - 4.46$$

where T is the absolute temperature Centigrade, t°C. + 273.

As regards the action of ferric oxide as a catalyst, the following results were determined by Lunge and his pupils:

(1) The conversion is practically the same with gases containing from 2% to 12% by volume of sulfur dioxide.

(2) The gaseous mixture must be as dry as possible.

(3) Exposure of the iron oxide to moist air reduces its activity.

(4) Porous ferric oxide is better than the dense material, e. g., pyrites cinders is suitable.

(5) The addition of cupric oxide improves the catalytic activity of the ferric oxide.

(6) Arsenic trioxide is completely retained by the contact mass at about 700°.

(7) The optimum temperature for operation is from 600° - 620°. The reaction begins at about 400°, and the maximum conversion at the optimum temperature of 620° is 60%.

(8) Arsenic pentoxide alone has a marked catalytic activity.

As Haber remarks, the practical yield may be in excess of the calculated, because the gases may come in contact with the catalyst in cooling down, and advantage thus be taken of the in-

1. "Thermodynamics of Technical Gas Reactions," 1908, 199. See also F. Zeisberg, Trans. Amer. Electrochem. Soc. 1919, 195; abst. J. S. C. I. 1920, 39, 104-A.

2. "Alkali Industry," 42.

creased yield which is readily obtainable at lower temperatures.

Knietsch's results may be summed up in the statement that, so far as the velocity is concerned, the range of temperature below 200° may be regarded as one in which no reaction takes place; between 200° and 450° the reaction of formation of sulfur trioxide prevails; above 450° the rate of decomposition of sulfur trioxide is predominant; and above 900° practically no sulfur trioxide at all is formed. The temperature of reaction is lowest with the platinum catalyst, hence this metal is most suitable. With ferric oxide, the formation of sulfur trioxide is appreciable only at about 600° , when the reverse reaction, leading to its decomposition, is already quite marked. It is therefore necessary to complete the conversion by passing the gases, after they have gone through the ferric oxide converter, through a platinum catalytic mass, as has been explained.

The Badische Process. Before describing the more recent methods of operating the contact process,¹ an account of the methods and apparatus used by the Badische Anilin und Soda Fabrik, which was initiated by the patents taken out in 1901, but resulted from many years of experiment, may be given, since these patents embody practically all the essential details of the use of a platinum catalyst with the purification of the gases, which have appeared in later specifications, the latter containing only unessential improvements in the apparatus.

Large-scale operations were made possible by the discovery in 1898² of methods of purification of the initial gases. These have already been briefly considered (p. 1089). The principal impurities are arsenic, phosphorus, mercury, sulfuric acid and sulfur, and dust of any kind. These are separated by treating the gases while hot with a jet of steam, with or without air or other gas, then gradually cooling, and afterwards repeatedly washing and finally drying by means of sulfuric acid. The gases after purification may be considered suitable if they are optically pure, i. e., exhibit no scattering of light when a beam of the latter is passed through them. The path of the light should be absolutely invisible as it passes through the gas. This is a very severe test

1. G. Friedlander, *Rev. prod. chim.* 1918, **21**, 22; *abst. C. A.* 1918, **12**, 1688; *Chem. Zentr.* 1919, **90**, II, 53.

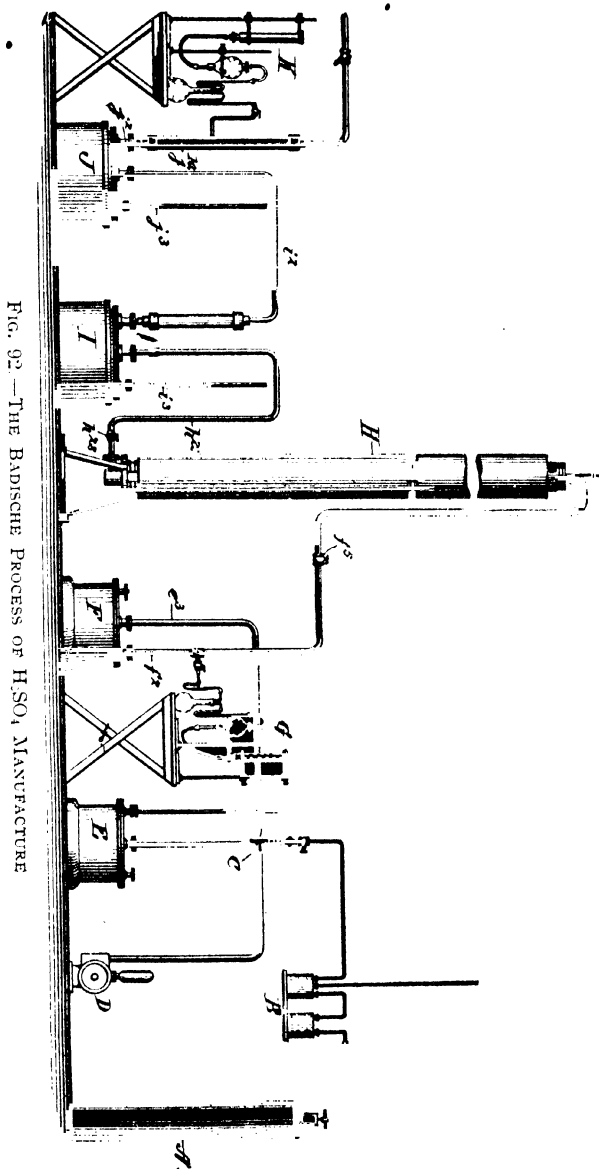
2. Badische Anilin u. Sodafabrik, *E. P.* 15948, 1898; *abst. J. Soc. Dyers Col.* 1899, **15**, 254.

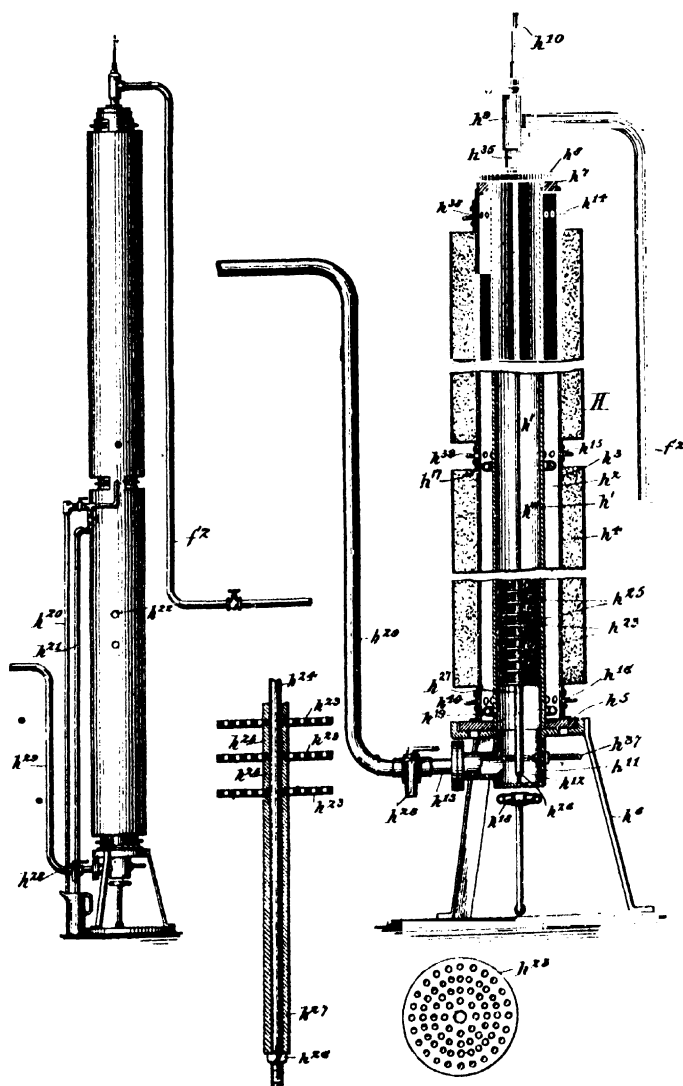
of the purity of the gas, as a gas which is apparently pure to chemical tests, and appears quite clear in ordinary transmitted daylight, may contain traces of fog, which appear as a luminous haze when a beam of light is passed through the gas, and in this case would sooner or later lead to poisoning of the catalyst. The purification of the gases is described in more detail in the later specification of 1902,¹ the apparatus being shown in Fig. 92. The sulfur dioxide passes from the supply *A* through the drying train *B*, and then into a mixer *C*, in which the gas is mixed with air from the pump *D*. It appears that the use of pure sulfur dioxide gas is contemplated. The mixed gases pass to a washer *E*, which is a leaden vessel from the top of which is suspended a serrated hood, dipping into sulfuric acid of 66° Bé. A pressure gauge connected with the entrance and exit show the respective pressure. The gases next pass to the stripper *F*, similar to the washer but containing no liquid. The purpose of this is to remove sulfuric acid carried over from the washer. The gases next pass to the contact apparatus *H*, to be described later, the sulfur trioxide formed therein being taken up by sulfuric acid of 66° Bé.

The absorber is provided with a serrated hood in the same way as the washer. The second absorber *J*, is of cast iron, and contains sulfuric acid of 58° Bé., which is strengthened to 66° Bé. and then passed to the first absorber. *G* and *K* are testing apparati.

The contact furnace *H* (Fig. 93) consists of a central tubular contact chamber *h*₁, jacketed by the annular passage *h*₂ and surrounded by the insulating material *h*₃. The sheet-iron tube *h*₃, forming the annular passage, is pierced to form a series of port-holes, *h*₁₄, *h*₁₅ and *h*₁₆, each series being provided with two independent circular covers governing separate halves of the series, *h*₃₈, *h*₃₉ and *h*₄₀, by which the admission of air for regulating the heat is controlled, the heat being supplied from the gas-burner *h*₁₉ and annular burners *h*₁₇ and *h*₁₈. The mica-covered peep-holes *h*₂₂ enable observation to be made of the temperature, which should be a dull red opposite the upper portion of the

1. E. P. 15947, 1898; abst. J. Soc. Dyers Col. 1899, **15**, 254. E. P. 12781, 1901; abst. J. Soc. Dyers Col. 1902, **13**, 197; J. S. C. I. 1902, **21**, 772. U. S. P. 692018, 1902; abst. J. S. C. I. 1902, **21**, 345; Chem. Zts. 1902, **1**, 708; J. A. C. S. 1902, **24**, 281; Mon. Sci. 1902, **58**, 73.

FIG. 92.—THE BADISCHE PROCESS OF H_2SO_4 MANUFACTURE

FIG. 93.—THE BADISCHE CONTACT PROCESS FOR H_2SO_4 MANUFACTURE

contact material. The temperature is regulated by thermometers at h_{16} , h_{14} and h_{37} .

In the contact material holder, the rod h_{24} , removable from the top on withdrawing the cover h_8 has strung upon it a series of wrought iron plates h_{23} , distanced by sections of piping, h_{25} , and the bottom plate is distanced by the nut h_{26} , on the bottom of the rod by the section of piping h_{27} . This latter section, in charging the apparatus, is dropped down the rod, followed by a perforated plate, on which is scattered a certain quantity of 10% platinized asbestos; one of the piping sections is then dropped into position, and a perforated plate, and so on until the apparatus is charged. The process and apparatus was stated to accomplish an average conversion of 95.9%, with gases containing 11.5% of sulfur dioxide.

It is apparent that this apparatus is nothing but a laboratory arrangement, and is not adapted to large scale working, and that it requires the use of pure sulfur dioxide, since no arrangement is described for the purification of the gases beyond mere drying.

The absorption of the gases in sulfuric acid, the first absorber comprizing sulfuric containing at least 27% free SO_3 , in a vessel of wrought iron, and the second ordinary acid,¹ and an alternative process² in which a cast iron apparatus charged with 98% sulfuric acid, the strength of which is maintained constant by admitting steam, water, or dilute sulfuric acid, are disclosed.

The preparation of the catalyst is described,³ and the regulation of the temperature by using an annular space between the catalyst tube and the tube bringing in the cold gases⁴ are also referred to.

The first real description of the process occurs in the important patents of 1900.⁵ In this reference is especially directed to the importance of regulating the temperature during the reac-

1. E. P. 1904, 1901; abst. J. S. C. I. 1902, **21**, 116; J. Soc. Dyers Col. 1902, **18**, 49. E. P. 6829, 1901; abst. J. S. C. I. 1902, **21**, 344; J. Soc. Dyers Col. 1902, **18**, 114.

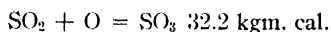
2. E. P. 6828, 1901; abst. J. S. C. I. 1902, **21**, 344; J. Soc. Dyers Col. 1902, **18**, 114.

3. E. P. 6828, 1901; 6829, 1901; abst. J. S. C. I. 1902, **21**, 344; J. Soc. Dyers Col. 1902, **18**, 114. D. R. P. 133933 abst. Zts. ang. Chem. 1902, **15**, 935.

4. E. P. 15949, 1898; abst. J. Soc. Dyers Col. 1899, **15**, 245.

5. R. Knietzsch, U. S. P. 774083, 1904; abst. J. Soc. Dyers Col. 1905, **21**, 24; Mon. Sci. 1905, **63**, 55; J. A. C. S. 1905, **27-R**, 432. U. S. P. 652119, 1900.

tion so the heat which is evolved in the exothermic reaction:



shall not be allowed to heat up the contact mass to such a high temperature as to lower the equilibrium yield. It is stated that the rise of temperature of the contact mass during operation is the chief cause of the non-success of previous attempts, and that the discovery of this fact was novel. This can hardly have been the case, since the dependence of the equilibrium on the temperature was obvious from the exothermic nature of the reaction, from the law of Le Chatelier, which was known before Knietzsch published his work. What was new, were the forms of apparatus used to effect the regulation of the temperature, although here again a well known principle of heat-interchange was used. In the apparatus employed, the excess of heat of reaction is removed from the converted gas as it is passing through the reaction chamber by the absorption of such heat by the gas which is about to be converted, by causing the whole or a portion to pass within heat absorbing proximity to the converted gas in the apparatus itself.

Two forms of apparatus specified are indicated in Figs. 94 and 95. In Fig. 94 appears an apparatus provided with a number of tubes containing the contact substance, the heat of reaction being removed by the incoming gas on its way to the contact tubes. The apparatus also contains arrangements whereby the incoming gas current may be directed along and against the outside of the contact tubes and for mixing the gases before entry to these tubes. Fig. 95 shows an apparatus in which the excess of heat is removed by the incoming gas current on its way to the ingress end of the contact tube. The lettering in the two figures refers to similar parts.

M is an enclosure, which may consist of brickwork or iron pipe. *R* is the contact chamber or chambers, shown in the form of a tube or tubes supported at one end by the tube-plate *W* and at the other end by the tube-plate *W'*. *S'* is an air passage surrounding the contact tubes from end to end, having an inlet *n* at one end and an outlet *L* at the other end. *h h* are means of heating the air current at or near the entrance of the passage *S'*, and capable of regulation, such as a series of gas-burners. The current of air in the passage *S'* may serve as a medium for initiating

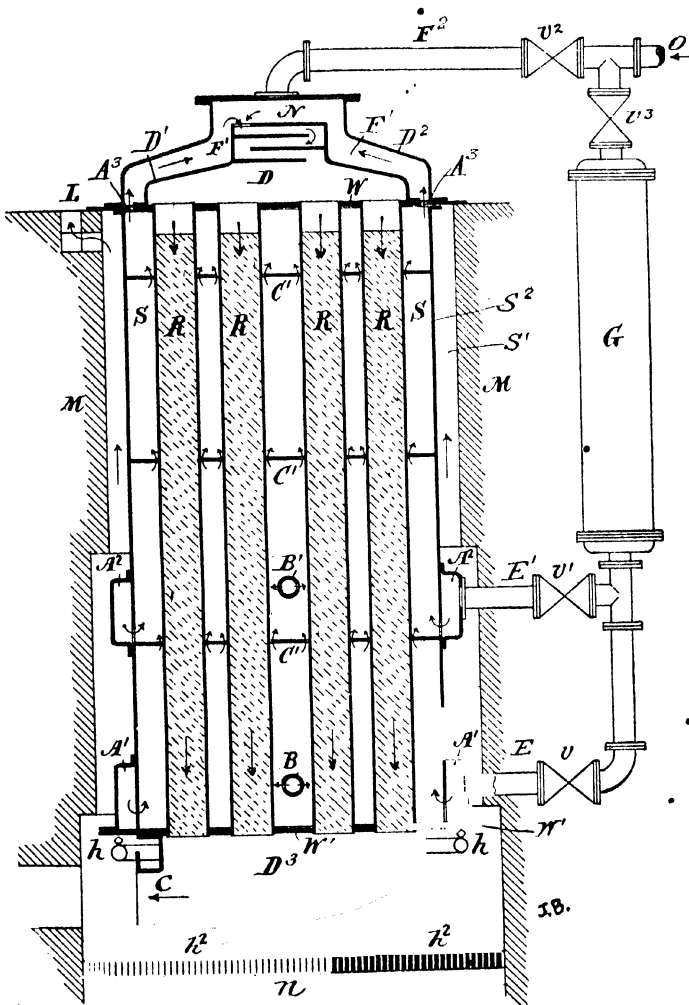


FIG. 94.—THE BADISCHE CONTACT FURNACE

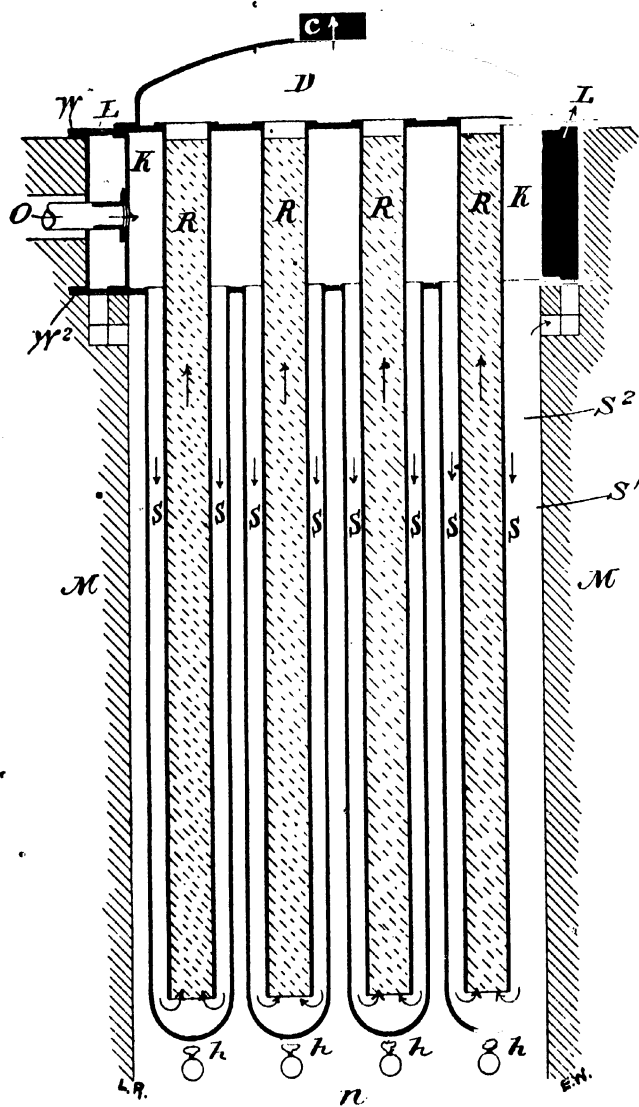


FIG. 95.—THE BADISCHE CONTACT FURNACE

the reaction and as a medium for cooling when the reaction is in progress. S is a passage surrounding the contact tubes, by which the gas mixture passing to the catalyzer is conducted and kept in contact with the tubes R from end to end. S_2 is a tube secured to the tube-plate W , and separating the passages S and S' . c is a passage receiving the sulfur trioxide at the outlet end, and conducting it away from the apparatus. O is a pipe leading to the apparatus from the source of the mixed initial gases. v, v', v_2 , etc., are valves for regulating the supply of gas to the various pipes. G is a heater for heating the initial gas mixture. The contact substance is placed in the tubes R in a manner already described.

In order to direct the passage of the cooling gas, a number of baffles, C, C' , are placed within the chamber S in such a way that in passing them the gases are compelled to pass close to the walls of the tubes R . The mixing apparatus N serves to mix the gases before entrance to the catalyzer tubes, so as to equalize the temperature. The cover is made in two parts, D_1 and D_2 , with the mixer N placed in the opening at the center of D_1 , through which the gases must pass in proceeding from the openings A_3 , located at the end of the chamber S , and outside the tubes R . The gas then passes inwardly through the passages F_1 and down to the entrance of the tubes R . The temperature of the gases is noted by thermometers placed inside the covers D and D_3 .

In Fig. 94 a number of tubes are used with tubular pockets S_2 , extending through an additional tube-plate W_2 , so as to form a box-like chamber K between the tube-plates W and W_2 , into which the entering gases pass from the pipe on its way to the top of the tubular pockets S_2 , and the space in K serves for the distribution of the entering gases. The gases stream through the space S and cool the contact substance in R .

The mode of procedure is described as follows: It is supposed that a mixture of gases containing about 12% by volume of sulfur dioxide and a similar amount of oxygen is taken, the balance consisting of nitrogen. The apparatus is first heated by the gas burners until a thermometer in the upper cover D indicates a temperature of about 300°. The source of heat is then cut off, and the entire stream of gas passed into the apparatus at A' . The temperature within the cover D first rises. When it has

reached a temperature favorable to the reaction, the upper valve v_2 is opened, so that a part of the gas enters directly through F_2 . The gases entering and leaving the apparatus are analyzed to determine their contents of sulfur dioxide, and in this way the conversion is determined. The temperature in the inside of the contact apparatus is regulated by the reading of the thermometers in D and D_3 by so arranging the cooling stream of gas and the intensity of the current by means of the valves v , v' and v_2 and the temperature, if necessary, by means of the heater G , that "the most favorable conversion of the gas into sulfuric anhydride is achieved." In the case cited about two-thirds of the entire gas current is admitted at A' and one-third direct through F_2 into D , so that the temperature in D , which becomes uniform, owing to the action of the mixing chamber N , is about 380°C ., while the thermometer in D_3 actually registers about 234°C . The conversion is stated to be 96% to 98% of that theoretically possible, while making from forty to fifty kgm. SO_3 per pipe per 24 hours. The dimensions of the pipes are given as about 7 ft. long by 5 in. diameter. The conversion can be increased to 99% if the gases are allowed to remain longer in contact with the catalyst. (These values presumably refer to percentages of the theoretical *equilibrium* yields, not to the over all conversion.) The special features of the process are stated to be cold entering gases, no external sources of heat, and gases leaving the apparatus at a temperature considerably below the temperature of reaction.

Additional patents¹ were issued in 1901, but these contain no new matter, being merely divisions of the patent of the year previous, in order to obtain protection for specific apparatus. A patent of 1904 refers to platinized asbestos spread on perforated plates in a tube, as has already been explained, (p. 1141).

A patent of 1905² refers to the absorption of sulfur trioxide in sulfuric acid containing about 27% of free sulfur trioxide in wrought iron vessels, whereby an acid containing only 0.003%,

1. U. S. P. 688020, 1901; abst. Chem. Zts. 1902, **1**, 479; J. A. C. S. 1902, **24**, 261; Mon. Sci. 1902, **58**, 71. U. S. P. 688469, 1901; abst. J. A. C. S. **24**, 262; Mon. Sci. 1902, **58**, 72. U. S. P. 690062, 1901; abst. J. S. C. I. 1902, **21**, 253; Chem. Zts. 1902, **1**, 580; J. A. C. S. 1902, **24**, 338; Mon. Sci. 1902, **58**, 73.

2. U. S. P. 800218, 1905; abst. J. A. C. S. 1905, **27R**, 232; Mon. Sci. 1906, **65**, 19.

iron, or less is usually obtained when operating the process.

In 1906 three patents were published.¹ In the first, an improvement of the process described in 1900 and 1902 is specified, which consists in subdividing the conversion, previously carried out in one operation with the aid of 50% platinized asbestos, into two or more stages, carried out in separate contact chambers, and absorbing the sulfur trioxide formed in each stage before passing the gas to the converter following. In this way the back-reaction due to the action of mass of the sulfur trioxide is eliminated, since the only sulfur trioxide which comes in contact with the catalyst in each stage of the process is that formed in that stage alone. In this way an economy of platinum is effected, the amount of platinum in each contact chamber (when two chambers are used in the manner indicated) being only one-fourth of that employed in a single contact chamber effecting the conversion in one stage. The arrangement of the apparatus calls for no special mention. It consists of a number, say two, of contact chambers of the type previously described, with an absorption apparatus between each pair of contact chambers. A higher conversion may thus be effected without increasing the amount of platinum.

In the second patent an absorption apparatus is described. This (Fig. 96) is similar to that used in the absorption of ammonia for the production of ammonium sulfate. In the figure, 1 is a cast-iron enclosure from the top of which is suspended a cast-iron hood 2, the lower edge of which is serrated. The pipe 3, supplying the sulfur trioxide is connected with the top of the hood. The exit pipe 4 leads from the top of the enclosure 1. The vessel 1 is supplied with sulfuric acid through a stand-pipe 5, extending to near the bottom of the enclosure, the level of the acid in the latter being kept above the teeth of the hood. The finished product is drawn off by the cock 6. The vessel 1 is enclosed in an iron tank 7 containing water for cooling the absorption acid, the water entering through the pipe 8 and leaving through the pipe 9. There are pressure gauges, 10 and 11, on the inlet and outlet pipes, respectively. The outlet pipe 4 should be

1. U. S. P. 809450, 1906; abst. Chem. Zts. 1906, **5**, 135; J. A. C. S. 1906, **28R**, 415; Mon. Sci. 1906, **65**, 115. U. S. P. 816918, 1906; abst. J. A. C. S. 1906, **28R**, 520; Mon. Sci. 1906, **65**, 116. U. S. P. 823472, 1906; abst. Chem. Zts. 1906, **5**, 400; J. A. C. S. 1906, **28R**, 623; Mon. Sci. 1907, **67**, 12.

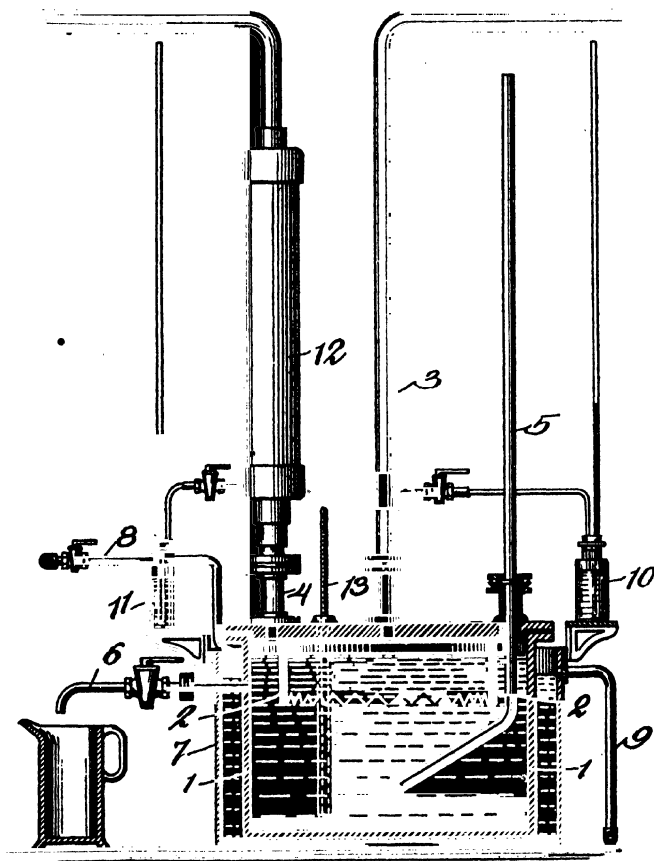


FIG. 96.—THE BADISCHE PROCESS OF SO_3 MANUFACTURE

wholly or partially of larger diameter as at 12, to allow the unab-sorbed gas to deposit liquid mechanically carried over, which runs back into the vessel 1. The thermometer 13 registers the tem-perature in 1. In the operation of the apparatus, 1 is charged with sulfuric acid of about the strength of the finished product, acid of lower strength being used to replenish the vessel through the pipe 5. The weaker acid is supplied in such quantities that, owing to absorption of sulfur trioxide, the liquid acid is main-tained at its original strength throughout the operation. The best strength is stated to be 97% to 99% H_2SO_4 .

The third patent relates to the arrangement of the catalytic material in the contact tubes. In this (Fig. 97) the tubes are

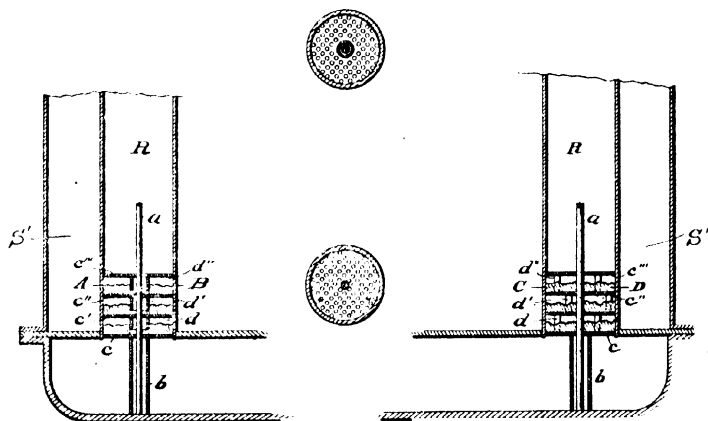


FIG. 97.—BADISCHE PROCESS FOR PRODUCING SULFUR TRIOXIDE

divided into a number of compartments by the insertion of per-forated plates, upon each plate being laid a layer of contact ma-terial sufficient to cover it. With a tube of 4 in. diameter and a space between the plates of one-tenth of an inch, each layer may consist of about ten grams of 10% platinized asbestos. The layers are thus relieved in whole or in part of pressure upon each other, while the gas shall have no other course save through the contact mass. In the sketch, *a* is an iron rod suitably supported at the bottom of the contact tube *R* and passing up its central line. Over this rod a narrow tube *b* may be placed, reaching up

to the rod to the elevation of the lower end of the contact mass in the contact tube. The first perforated plate *c* is then passed down the contact tube over the rod *a* and rests upon the narrow tube *b*. Upon this plate sufficient platinized asbestos or similar contact mass is placed to cover up the perforations and periphery. Next a bead or short piece of narrow tube *d* is passed down the contact tube over the rod *a* until it is supported by the perforated plate *c* or a portion of the contact material resting upon it. Another perforated plate *c'* is then placed in position to rest on the bead or tube *d*, and is covered by a layer of contact material. This process is continued until the tube is charged. The perforated plates may be supported by tripods *D*₃, *D*₄, *D*₅, instead of narrow tubes or beads, or other methods of supporting the plates may be used.

English patent 6828 of 1901 describes the use of other carriers for the platinum in place of asbestos. This is effected by the intermediate action of an intimate mixture of an oxide or hydrate of a fixed alkali or alkaline earth, or salts of these containing a volatile acid such as hydrochloric, acetic or carbonic, with a salt of a volatile base such as ammonia, and a less volatile acid as sulfuric or phosphoric, at a suitable temperature. Double decomposition takes place, the vapor of the volatile salt found imparting a high degree of porosity to the non-volatile salt either before or after heating. The oxides of iron, copper or chromium are also specified as substrata for platinum black.¹ Thus 145 parts of burnt pyrites entirely free from arsenic, in pieces about the size of a pea, screened free from dust, are impregnated with 30 parts of a solution of platinic chloride containing 17 gm. per liter. The resulting mass can be used at once, or may first be heated.

In a later specification the use of vanadium pentoxide,² prepared by heating a mixture of 200 parts of finely ground pumice powder with 14 parts of ammonium vanadate, moulded into the required shape, to 300° to expel ammonia, and then to 440° in a current of sulfur dioxide to produce cohesion, or similar catalysts containing vanadium pentoxide, is specified. These are stated to

1. D. R. P. 140353; E. P. 10729, 1901.

2. E. P. 23541, 1913; abst. J. S. C. I. 1915, **34**, 823; Ann. Rep. Chem. Ind. Soc. 1916, **1**, 112. E. P. 8462, 1914; abst. J. S. C. I. 1915, **34**, 822. D. R. P. 291792; abst. Zts. ang. Chem. 1916, **29**, 270; Chem. Zentr. 1916, **87**, I, 1048; Chem. Ztg. 1916, **40**, 211.

possess activity almost equal to that of platinum. The alkaline salts of osmic and ruthenic acids,¹ supported on asbestos, magnesia, alumina, pumice and meerschauum, also have been proposed. Zeolite² or sodium aluminium silicate ("Permutit") may also be impregnated with solutions of potassium chloroplatinate, osmate, or ruthenate, or tungsten chlorides.³

The Tentelew Process, issued in the names of G. Eschellmann and A. Harimuth on behalf of the Tentelew Chemical Works of Petrograd,⁴ refer to a contact process using platinum, but differ-

1. D. R. P. 292242; abst. Zts. ang. Chem. 1916, **29**, 292; Chem. Ztg. Rep. 1916, **40**, 213. E. P. 12977, 1913; abst. C. A. 1914, **8**, 3842; J. S. C. I. 1914, **33**, 483; Mon. Sci. 1917, **84**, 37. E. P. 1358, 1915; abst. J. S. C. I. 1916, **35**, 689; Ann. Rep. Chem. Ind. Soc. 1916, **1**, 121.

2. Norw. P. 26822.

3. For further information on this process consult the following patents, all of which were taken out by the Badische Co.: U. S. P. 688470; abst. J. A. C. S. 1902, **24**, 262; Mon. Sci. 1902, **58**, 72. U. S. P. 688471; abst. J. A. C. S. 1902, **24**, 262; Mon. Sci. 1902, **58**, 72. U. S. P. 688472; abst. J. A. C. S. 1902, **24**, 262; Mon. Sci. 1902, **58**, 72. U. S. P. 692018; abst. J. S. C. I. 1902, **21**, 345; Mon. Sci. 1902, **58**, 73; Chem. Zts. 1902, **1**, 798; J. A. C. S. 1902, **24**, 281. U. S. P. 822373; abst. J. A. C. S. 1906, **28R**, 539. E. P. 15950, 1898; abst. J. Soc. Dyers Col. 1899, **15**, 251. E. P. 10729, 1901; abst. J. S. C. I. 1902, **21**, 548; Chem. Ztg. 1902, **26**, 929; Mon. Sci. 1903, **59**, 75. D. R. P. 113932; abst. Zts. ang. Chem. 1900, **13**, 1037; Chem. Centr. 1900, **71**, II, 792; Jahr. Chem. 1900, **53**, 218; Chem. Zts. 1902, **1**, 13; Chem. Ztg. Rep. 1900, **24**, 952; Wag. Jahr. 1900, **46**, I, 301. D. R. P. 113933; abst. Zts. ang. Chem. 1900, **13**, 938; Chem. Centr. 1900, **71**, II, 793; Jahr. Chem. 1905-1908, II, 1617; Chem. Zts. 1902, **1**, 13; Chem. Ztg. 1900, **24**, 778; Wag. Jahr. 1900, **46**, I, 310. D. R. P. 119059; abst. Chem. Centr. 1901, **72**, I, 865; Jahr. Chem. 1901, **54**, 241; Chem. Zts. 1902, **1**, 13, 305; Chem. Ztg. 1901, **25**, 381; Wag. Jahr. 1901, **47**, I, 415; Mon. Sci. 1901, **57**, 211. D. R. P. 133713; abst. Zts. ang. Chem. 1902, **15**, 935; Chem. Centr. 1902, **73**, II, 773; Chem. Zts. 1903, **2**, 274, 529; Chem. Ztg. 1902, **26**, 878; Wag. Jahr. 1902, **48**, I, 283. D. R. P. 133933; abst. Zts. ang. Chem. 1902, **15**, 935; Chem. Centr. 1902, **73**, II, 773; Jahr. Chem. 1902, **55**, 355; Chem. Zts. 1903, **2**, 219, 274; Chem. Ztg. 1902, **26**, 850; Wag. Jahr. 1902, **48**, I, 284. D. R. P. 133247; abst. Zts. ang. Chem. 1902, **15**, 764; Chem. Centr. 1902, **73**, II, 410; Jahr. Chem. 1902, **55**, 357; Chem. Ztg. 1902, **26**, 708; Wag. Jahr. 1902, **48**, I, 280, 285; Mon. Sci. 1903, **59**, 106; Chem. Zts. 1903, **2**, 274. D. R. P. 150353; abst. Zts. ang. Chem. 1904, **17**, 823; Chem. Centr. 1904, **75**, 1117; Chem. Ztg. 1904, **28**, 603; Wag. Jahr. 1904, **46**, II, 473. D. R. P. 118196; abst. Zts. ang. Chem. 1904, **17**, 244; Chem. Centr. 1904, **75**, I, 410; Jahr. Chem. 1904, **57**, 460; Chem. Ztg. 1904, **28**, 65; Wag. Jahr. 1904, **46**, I, 289; Chem. Zts. 1904, **3**, 460, 504. D. R. P. Ann. B-74226. F. P. 280647, 280648, 280649; abst. Mon. Sci. 1899, **54**, 133, 649, 652, 654. F. P. 309673; abst. Mon. Sci. 1902, **58**, 169. F. P. 414387; abst. C. A. 1912, **6**, 1965; Chem. Ztg. Rep. 1910, **34**, 498; Mon. Sci. 1913, **79**, 79. Belg. P. 137751, 137752, 137753, 158923. Aust. P. 1093, 1662, 1771, 10675; abst. Chem. Zts. 1903, **2**, 347. Russ. P. 5842, 5897, 5945, 8504. Hungarian P. 15503, 15475, 25533, 25574. Swiss P. 17826, 1898.

4. The following patents were taken out by the Tentelew Chemical Co.: U. S. P. 792205, 1905; 900500, 937147; 937148; abst. Mon. Sci. 1910, **73**, 82. U. S. P. Re-12759, 1908. E. P. 3327, 1891; 11969, 1902; abst.

ing in many respects from that of the Badische Co. Distinctions in the purification of the burner gases between the two processes are as follows:

| Badische | Tentelew |
|--|---|
| 1. Steam is added to the hot burner gases. | 1. No steam is added to the gases. |
| 2. The gases are cooled. | 2. The gases are cooled. |
| 3. The gases are not filtered. | 3. The gases are subjected to dry-filtration for removal of acid fog. |
| 4. The gases are washed with sulfuric acid to remove acid fog. | 4. The gases are not washed with sulfuric acid. |
| 5. The gases are not treated with alkali. | The gases are washed with an alkaline liquid to remove chlorine, fluorine, etc. |

The contact apparatus of the Tentelew process differs in a number of essential respects from that of the Badische. In the process as actually in use, however, the apparatus differs markedly from that of the patent specifications, so that it appears unnecessary to describe the latter at length. The Tentelew apparatus is especially useful in completing the conversion partially effected by the iron oxide catalyst of the Mannheim process, and as so used the apparatus is of a very simple character. The gases from the Mannheim plant, after the sulfur trioxide has been absorbed in sulfuric acid towers, are carefully filtered and freed

J. S. C. I. 1903, **22**, 695. E. P. 20952, 1904; abst. J. S. C. I. 1905, **24**, 496. E. P. 22095, 1907; abst. J. S. C. I. 1908, **27**, 280. E. P. 23419, 1909; abst. J. S. C. I. 1910, **29**, 422. F. P. 321275, 1902, and addition 3778 thereto; abst. Mon. Sci. 1903, **59**, 125. F. P. 382081, 1907; 407914, 1909. D. R. P. 178762, 1904; abst. Zts. ang. Chem. 1907, **20**, 1066; Chem. Zentr. 1907, **78**, I, 431; Jahr. Chem. 1905-1908, I, 1624; Zts. Schiess. Spreng. 1907, **2**, 12; Chem. Ztg. Rep. 1906, **30**, 475; Wag. Jahr. 1906, **52**, I, 378. D. R. P. 194176; abst. Zts. ang. Chem. 1908, **21**, 931; Chem. Zentr. 1908, **79**, I, 908; Jahr. Chem. 1905-1908, I, 1458; Chem. Zts. 1908, **7**, 758; Chem. Ztg. Rep. 1908, **32**, 94; Wag. Jahr. 1908, **54**, I, 368; Mon. Sci. 1910, **73**, 145. D. R. P. 211999; abst. Wag. Jahr. 1909, **55**, I, 347. D. R. P. 227095; abst. Zts. ang. Chem. 1910, **23**, 2190; Chem. Zentr. 1910, **81**, II, 1346; Jahr. Chem. 1910, I, 526; Zts. Schiess. Spreng. 1910, **5**, 441; Chem. Ztg. Rep. 1910, **34**, 550; Wag. Jahr. 1910, **56**, I, 421. D. R. P. 230585; abst. Zts. ang. Chem. 1911, **24**, 425; Chem. Ztg. Rep. 1911, **35**, 95. D. R. P. Anm. of Jan. 18th and Sept. 1910. D. R. P. 244838; abst. Wag. Jahr. 1912, **58**, I, 373. Aust. P. 15751, 1903; 21164, 1905; 32902, 1907; 43754, 1910. Belg. P. 163469, 1902; 179782, 1904; 199923, 1907; 219865, 1909. Hung. P. 26477, 1902; 32779, 1904; 41504, 1907; 49163, 1909. Italian P. 139/153; 189/196; 314/86; 187/261. Jap. P. appl. of Dec. 10, 1909. Norw. P. 11372, 13975, 20029. Roum. P. 141, 813, 1582. Russ. P. 6691, 6692, 1902; 8845, 1904; 10880, 1900; Russ. P. Appl. Oct. 20, 1909; Feb. 17, 1910. Span. P. 46563, 1910. Swed. P. 15967, 19742, 29437. Swiss P. 26495; abst. Chem. Zts. 1904, **3**, 21. Swiss P. 32699; abst. Chem. Zts. 1905, **4**, 400. Swiss P. 41769, 49757.

from fog by boxes containing coke moistened with strong sulfuric acid to which a little oleum is added. They are then re-heated in iron pipes and passed to a rectangular brickwork tower, containing iron frames (Fig. 98), in which the catalyst material is fitted. The catalyst material consists of asbestos cloths, like the ordinary sponge-cloths used for drying crockery, which have been impregnated with platinum by soaking in a solution of chloroplatinic acid and then reducing in a bath of sodium formate, as

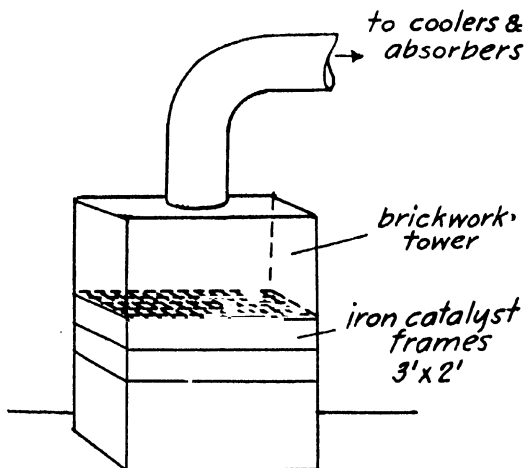


FIG. 98.— THE TENTELEW SULFURIC ACID CONTACT METHOD

previously described (p. 1113). Each asbestos mat measures about 3 ft. by 2 ft., and contains 40 grams of platinum. About 25 mats are superposed one above the other, in contact, in the iron frame, which can be fitted in place or removed from the brickwork tower. The gases enter the Tentelw shaft at about 450° and issue at about 500° . The absorption of the sulfur trioxide is carried out in towers containing strong sulfuric acid, in the usual way. G. Lunge observes that, beyond a few patent specifications which he quotes, the process is kept with perfect secrecy, and that the preparation of the contact material, especially, is

a profound secret, although it would appear that the process is not intricate.

The filters described by the patent specifications are used as follows: The gases are first passed to a dust-chamber, provided with shelves, in which the coarser particles of dust are retained. They now pass into a space cooled by water where more dust is retained in the shape of soft mud, and much of the sulfuric acid fog condensed to acid of about 52° Bé., which runs away continuously. To remove fine dust and sulfuric acid fog, the gas now passes from the bottom upwards through a large coke filter, containing graded coke, finer towards the top, where the pieces are about 10 mm. diameter. In this "coarse filter" most of the acid condenses to acid of 40° Bé., and mud and dust carried over are retained. The filter is purified by forcing water up brick channels, on which the coke rests, two such filters being used. The gas next passes to the "fine filters," of which there are two, one only being used at a time. These are packed with much finer coke, the smallest pieces being 1 mm. diameter. The gas enters from the top, and cleaning, which is necessary about once per annum, is carried out by removing and replacing the top layers. The gases are now, according to the specification, passed to a series of washers, containing an aqueous solution of an alkali, or milk of lime, which remove chlorine, sulfuric acid fog, and fluorine. They are finally dried and passed to the contact apparatus.

A special apparatus for cooling the hot burner gases is described, consisting of a cylindrical cooling chamber with a preliminary chamber into which the gases enter, at the bottom of which is a collecting chamber open at the bottom, with an outlet for the cooled gases and dipping into a trough where the acid collecting forms a hydraulic seal. The chamber is built up of a number of rings, the flanges being soldered together. Each ring contains a number of hollow plates kept in place by stays. The chambers are surrounded by an outer mantle provided with an inlet for cooling water, and an outlet for the same. The cooling plates communicate at the top and bottom by rows of slits, the top side of the cooling plates being inclined from the inside outwards.

The preliminary chamber and the collecting chamber are also built up of rings. There is provided a number of branch pipes

for inlet of water. The mantle is made of wrought iron, all other parts of pure cast-lead, and the whole rests on a cast-iron ring. The cooling plates are stiffened by numerous cross-stays, and the rings by ribs.

The hot gas enters the apparatus and passes between the cooling plates. Cooling water enters at the bottom into the mantle and rises through the cooling plates, the condensed acid falling into a trough *g*. The cooler is cleaned by introducing water through the necks at the top, and carries down the mud from the cooling plates into a trough. The gases enter at 500°, and are cooled to atmospheric temperature by a single passage through the apparatus.

The contact apparatus described consists of a cylindrical chamber forming what is called an "equalizing space," i. e., a space into which heat can be radiated from the contact material so as to keep down the temperature of the latter, with a cover and a gas-inlet. A smaller lower chamber is connected with the above by a conical connection, the gases being thoroughly mixed by passing through a central opening. A sieve-plate is provided, composed of several pieces, which serves to mix the gases. The principal portion of the contact mass, e. g., platinized asbestos, is spread over the plates in a layer reaching nearly to the tops of the cones. The contact plates may be taken out separately if the apparatus is to be repaired. The cones are supposed to take heat from the contact mass and radiate it out into the gases above. The plate also removes heat by conduction to the cones. The reaction is completed by passing the gases through a number, say 25, of layers of catalyst material.

In connection with the contact chamber is a regulator, or heat changer, the function of which is to effect an exchange of heat between the inlet gases, after cooling and purification, and the hot gases leaving the converter, this being of the usual multi-tubular type.

The absorbing tower is shown in Fig. 99, and consists of a number of superposed chambers *a*, *a*₁, *a*₂, each containing a specially shaped gas inlet pipe, *b*, surmounted by a hood, *c*, connected with the walls of the chamber, and perforated on the margin *d*. The gases are thus spread uniformly over each section of the tower. The chambers are surrounded by cooling jackets,

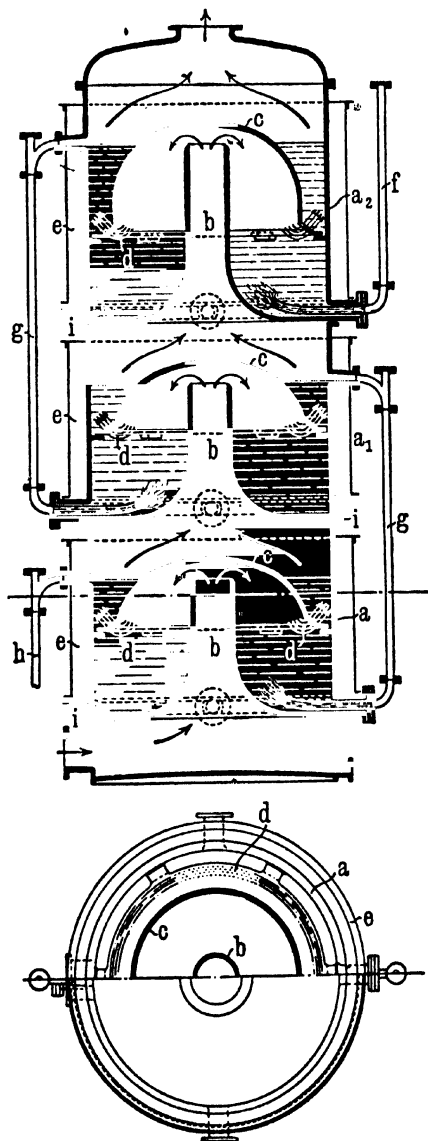


FIG. 99.—THE TENTELW PROCESS FOR SULFURIC ACID MANUFACTURE

e, through which water circulates. The hoods are arranged at such an angle that the liquid is thrown out against the cooled chamber sides. The absorbing acid is either introduced near the top at *f*, and flows through all the chambers by means of connecting pipes *g*, finally flowing away at *h*, or is introduced separately into each chamber. In the second method, acids of different strengths may be prepared.

The Meister, Lucius and Brüning Process. The process employed by the Farbwerke Höchst, vormals Meister, Lucius and Brüning, was invented by C. Krauss, and has been developed in various forms.¹

As a result of small scale experiments and theoretical considerations Krauss concluded that it was most advantageous to

1. The Farbwerke Höchst, vorm. Meister, Lucius & Brüning have taken out the following patents on the manufacture of sulfuric acid: U. S. P. 677670, 1901; abst. Mon. Sci. 1901, **57**, 281. U. S. P. 677692, 1901; abst. J. A. C. S. 1902, **24**, 137; Mon. Sci. 1901, **57**, 281. U. S. P. 700512; abst. J. S. C. I. 1902, **21**, 859; Chem. Zts. 1903, **2**, 274; J. A. C. S. 1902, **24**, 519; Chem. Ztg. 1902, **26**, 533; Mon. Sci. 1902, **58**, 184. E. P. 6057, 1898; abst. Mon. Sci. 1900, **56**, 12. E. P. 14728, 1898; abst. J. S. C. I. 1899, **18**, 584. E. P. 285, 1899; abst. J. Soc. Dyers Col. 1900, **16**, 22. E. P. 1385, 1901; abst. J. S. C. I. 1901, **20**, 1209. E. P. 2368, 1901; abst. J. S. C. I. 1902, **21**, 117; J. Soc. Dyers Col. 1902, **18**, 49. E. P. 3161, 1902; abst. J. S. C. I. 1903, **22**, 92; J. Soc. Dyers Col. 1903, **19**, 53. E. P. 4026, 1902; abst. J. S. C. I. 1903, **22**, 93. D. R. P. 105876, 1898; abst. Zts. ang. Chem. 1899, **12**, 1062; Chem. Centr. 1900, **71**, I, 445; Jahr. Chem. 1899, **52**, 424; 1900, **53**, 318; Chem. Ztg. 1899, **23**, 1063; Wag. Jahr. 1899, **45**, 361; Mon. Sci. 1902, **58**, 294; Chem. Zts. 1902, **1**, 13, 16. D. R. P. 109483, 1898; abst. Zts. ang. Chem. 1900, **13**, 397; Chem. Centr. 1900, **71**, II, 227; Chem. Ztg. 1900, **24**, 289; Wag. Jahr. 1900, **46**, I, 316; Mon. Sci. 1900, **56**, 185; Chem. Zts. 1902, **1**, 13, 16. D. R. P. 113932, 1899; abst. Zts. ang. Chem. 1900, **13**, 1037; Chem. Centr. 1900, **71**, II, 792; Jahr. Chem. 1900, **53**, 218; Chem. Ztg. 1900, **24**, 952; Wag. Jahr. 1900, **46**, 301; Mon. Sci. 1901, **57**, 115; Chem. Zts. 1902, **1**, 13. D. R. P. 119505, 1899; abst. Zts. ang. Chem. 1901, **14**, 445; Chem. Centr. 1901, **72**, I, 977; Jahr. Chem. 1901, **54**, 241; Chem. Ztg. 1901, **25**, 335; Wag. Jahr. 1901, **47**, I, 417; Mon. Sci. 1901, **57**, 211; Chem. Zts. 1902, **1**, 13. D. R. P. 135887, 1902; abst. Zts. ang. Chem. 1902, **15**, 1146; Chem. Centr. 1902, **73**, II, 1228; Jahr. Chem. 1902, **55**, 355; Chem. Ztg. 1902, **26**, 1061; Wag. Jahr. 1902, **48**, I, 287; Mon. Sci. 1903, **59**, 72; Chem. Zts. 1903, **2**, 274, 275. D. R. P. 139554, 1902; abst. J. S. C. I. 1903, **22**, 552; Zts. ang. Chem. 1903, **16**, 327; Chem. Centr. 1903, **74**, I, 856; Jahr. Chem. 1903, **56**, 344; Chem. Ztg. 1903, **27**, 306; Wag. Jahr. 1903, **49**, 252; Mon. Sci. 1904, **61**, 81; Chem. Zts. 1903, **2**, 528, 542. D. R. P. 169728; abst. Zts. ang. Chem. 1907, **20**, 974; Chem. Centr. 1906, **77**, II, 184; Jahr. Chem. 1905-1908, I, 1623; Chem. Ztg. Rep. 1906, **30**, 404; Wag. Jahr. 1906, **52**, I, 374; Mon. Sci. 1907, **67**, 146; Chem. Zts. 1907, **6**, 21. F. P. 318932, 1902; abst. J. S. C. I. 1902, **21**, 1454; Chem. Zts. 1903, **2**, 274; Mon. Sci. 1903, **59**, 122. Aust. P. 480, 1899; 12662, 1903; abst. Chem. Zts. 1903, **2**, 714. 29604, 1901. Belg. P. 134712, 1898; 136522, 1898; 140100, 1899; 154569, 1901; 161717, 1902. In this connection, see also Arndt, Dingl. Poly. 1907, **322**, 43; abst. C. A. 1907, **1**, 1460. M. Feigensohn, Chem. Ztg. 1906, **30**, 851. F. Winteler, Chem. Ztg. 1906, **30**, 87.

unevenly heat the contact mass, the temperature in the first zone of reaction being maintained sufficiently high to bring about rapid reaction of most of the sulfur dioxide, and then cooling the gases to about 400° , when the reaction is nearly complete. This gradation of temperature may be attained in either of two ways:

(1) By having a preliminary contact chamber maintained at a temperature of, say 530° , in which 75%-80% of the SO_2 is transformed into SO_3 , then cooling the gases to 400° , either by refrigerating tubes or by admixture with cold gases which do not disturb the process, and then passing to a second contact space, where the remaining 25% of SO_2 is converted into SO_3 .

(2) By employing a very long contact space, in which the gases enter at 530° , and gradually cool down to 430° before leaving.

The hotter contact space may be charged with cheaper contact substances, which are active at the higher temperatures, such as vanadic, molybdic and tungstic acids; oxides of iron, cobalt, nickel, copper, silver, manganese, chromium and uranium or oxides of rare elements such as cerium, didymium, lanthanum, zirconium, thorium, titanium, or even silica. Mixtures of the above catalysts may be used.

Among the metals of the platinum group, platinum only is sufficiently active, as iridium and palladium act but slowly, while gold is inactive.

Investigations of contact poisons have shown that mercury and carbon monoxide were innocuous. Sulfur, and water in the form of mist, or sulfuric acid mist, inhibit or stop the reaction. Arsenic, selenium, tellurium, and antimony are powerful contact poisons, selenium and tellurium causing permanent poisoning of platinum, while arsenic acts only temporarily and disappears in course of time, especially if the gases contain traces of moisture.

The arrangement of apparatus used is shown in Fig. 100. The pyrites burner gases issuing from the dust-chamber are cooled and purified in the arrangement R_1, R_2, R_3 , and then pass through a battery of pipes E in the dust-chamber where they are preheated by the hot burner gas. These pipes are arranged like an ordinary economizer with scrapers, gas passing through them being heated to 500° . The hot gases now enter the contact space O_1 , where most of the sulfur dioxide is converted into tri-

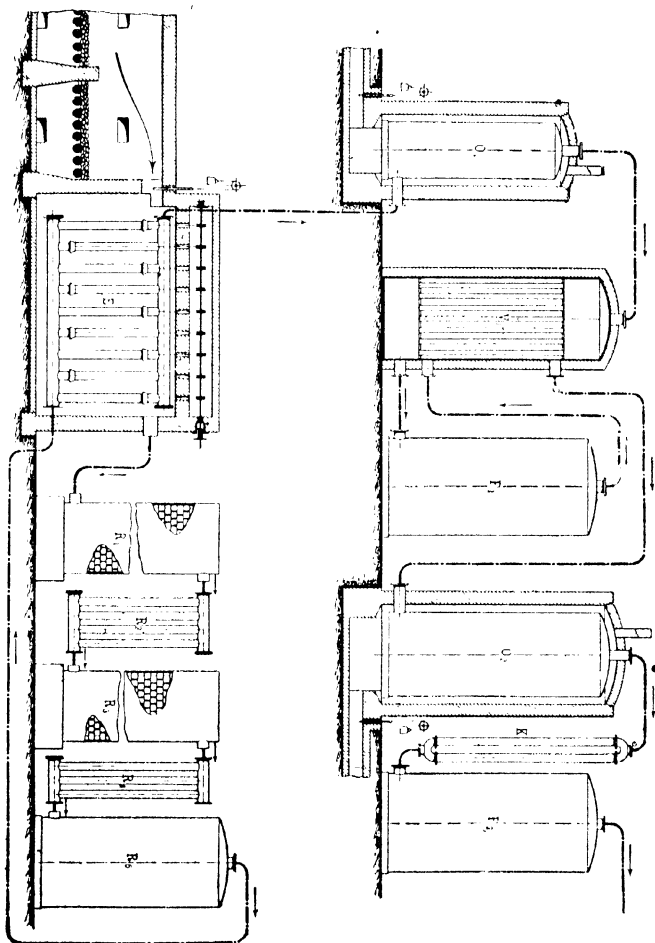


FIG. 100.—THE MEISTER, LEUCHS & BRÜNIG PROCESS OF CONTACT H_2SO_4 MANUFACTURE

oxide, and then pass to the heat interchanger V_1 , where they are cooled by gases passing in the opposite direction, the cooled gases being passed to the absorber F_1 , to remove the sulfur trioxide. The cooled gases pass back to the interchanger V_1 , if necessary through a special heat regulator, and into the contact space O_2 , where most of the remaining sulfur dioxide is converted into trioxide. The gases are cooled in K and the sulfur trioxide is retained in F_2 by strong sulfuric acid or by water or steam. Alternative processes are as follows:

(a) The kiln gases are cooled and purified in R_1, R_2, R_3 , heated by the exchanger V_1 and passed to the contact space O_2 , provided with a heat regulator, then back to V_1 , where they give up heat. After removing sulfur trioxide in F_2 the gases are heated in E , passed into O_1 , and absorbed in F_1 .

(b) The purified gases are heated in V_1 , passed through the contact space O_2 , cooled in K , freed from sulfur trioxide in F_2 , reheated in E , catalyzed in O_1 , passed through V_1 , and finally freed from trioxide in F_1 .

(c) The gases are purified in R_1, R_2, R_3 , heated in E , catalyzed in O_1 , cooled in K , freed from trioxide in F_1 , heated in V_1 , catalyzed in O_2 , passed back to V_1 , and freed from trioxide in F_2 .

In another process,¹ a rotary furnace C is used, fed with burnt pyrites impregnated with ferrous sulfate. The cylinder has longitudinal partitions which ensure that the material is turned over in its passage down the revolving cylinder. Gases from pyrites burners pass upwards through the same cylinder, and the burnt pyrites completely absorb the SO_2 at the cooler upper end of the cylinder. As the substance passes down to the hotter portions it is broken up, evolving SO_3 and leaving active ferric oxide, which induces combination of the SO_2 and oxygen in the gases passing over it. The ferrous sulfate is completely decomposed, and the sulfur in the burnt pyrites expelled, so that the spent substance falling into K_1 is free from sulfur.

The sulfur trioxide and sulfuric acid, with excess of nitrogen, passing out at the upper part of C are freed from dust in the chambers K_2 , and pass to the absorption apparatus. This process has been discontinued at Höchst.

According to the patent specifications, the platinum when

1. D. R. P. 139554, 1902; abst. J. S. C. I. 1903, **22**, 552; Zts. ang. Chem. 1903, **16**, 327.

poisoned with arsenic may be renovated by passing steam, mixed with hot burner gases, over them. When no more arsenic can be detected in the issuing gas, the steam is discontinued.

The absorbers used at Höchst are cast-iron vessels with outside cooling jackets. The gases are passed through the absorbing liquid in a state of fine division, induced by suction or pressure. If ordinary sulfuric acid is made, only one absorber is used, but for oleum two or three absorbers placed at different heights are employed. The absorbers are fed with acid containing more than 93% H_2SO_4 if oleum is made, but if ordinary acid is produced they are fed with dilute acid or even water. Up to 95% the acid is crystal-clear, but higher strengths are slightly turbid, from a little iron salts derived from the apparatus. These cannot be removed by settling or filtration, but disappear on the addition of a little water.

The Schroeder-Grillo Process.¹ The preparation of purified sulfur dioxide from pyrites burner gas, suited to the manufacture of sulfur trioxide by the contact process, was attained by the process of M. Schroeder and E. Haenisch in 1887.² This process has already been described under sulfur dioxide (p. 1092). It is, of course, too expensive for present day working. This gas, mixed with air in suitable proportions, was directed to be passed at a low red-heat, under pressure, over platinized asbestos. This

1. The Schroeder-Grillo process is covered by the following patents: U. S. P. 636924, 636925; U. S. P. 742502; abst. J. S. C. I. 1903, **33**, 1243; Chem. Zts. 1904, **3**, 244, 291; J. A. C. S. 1904, **26R**, 233; Mon. Sci. 1904, **61**, 31. U. S. P. 793543; abst. J. A. C. S. 1906, **28R**, 80; Mon. Sci. 1906, **65**, 19. E. P. 25158, 1898; abst. J. S. C. I. 1899, **18**, 584. E. P. 17034, 1900; abst. J. S. C. I. 1901, **20**, 579; Chem. Ztg. 1902, **26**, 94. E. P. 10412, 1901; abst. J. S. C. I. 1902, **21**, 344. F. P. 283496, 304530, 311689. D. R. P. 102244; abst. Zts. ang. Chem. 1899, **12**, 229; Chem. Centr. 1899, **70**, I, 1176; Jahr. Chem. 1899, **52**, 424; Chem. Ztg. 1899, **23**, 426; Wag. Jahr. 1899, **45**, 366; Mon. Sci. 1899, **54**, 145; Chem. Zts. 1902, **1**, 13. D. R. P. 115333; abst. Zts. ang. Chem. 1900, **13**, 1211; Chem. Centr. 1900, **71**, II, 1090; Jahr. Chem. 1900, **53**, 219; Chem. Ztg. 1900, **24**, 1000; Wag. Jahr. 1900, **46**, I, 325; Mon. Sci. 1901, **57**, 117; 1902, **58**, 293. D. R. P. 128554; abst. Chem. Centr. 1902, **73**, I, 737; Chem. Ztg. 1902, **26**, 251; Wag. Jahr. 1902, **48**, I, 291; Mon. Sci. 1902, **58**, 182; Chem. Zts. 1902, **1**, 609; 1903, **2**, 9. D. R. P. 138695; abst. Zts. ang. Chem. 1903, **16**, 186; Chem. Centr. 1903, **74**, I, 484; Chem. Ztg. 1903, **27**, 155; Wag. Jahr. 1903, **49**, I, 262; Chem. Zts. 1903, **2**, 529, 542. Aust. P. 565, 12287. Belg. P. 140984, 152713, 156974. Hung. P. 15502. Ital. P. 54742, 57464. Span. P. 25637, 26728. Swiss P. 22762; abst. Chem. Zts. 1902, **1**, 479. Russ. P. 8372, 8373, 8446. Natal P. 23, 156, 157, 1901. Cape Colony P. 1280, 1445, 1446. Patents have also been taken out in Chile and Peru.

2. E. P. 9188, 1887; abst. Chem. Centr. 1887, **58**, 1419.

process was discontinued when it became possible to use pyrites gases directly, as described by Knietsch. A proposal to use pyrites burner gas had been made in 1883 by W. Rath.¹

The history of the development of the very important modern Schroeder-Grillo contact process has been detailed by F. Meyer.² It originated in work carried out at Hamborn by the firm of Wm. Grillo, who were interested in the smelting of zinc blende, and the experimental work was carried out by Max Schroeder with a view to the utilization of the sulfur dioxide evolved in the roasting of the blende. The main objectives were to cheapen the contact process by utilizing the roaster gases directly, and to reduce the resistance of the contact material to the passage of the gases. Both conditions are fulfilled by the new contact mass proposed by M. Schroeder,³ which marks a distinct departure in the history of the contact process. In place of the insoluble materials previously used as carriers for the platinum, such as asbestos, pumice and burnt clay, Schroeder used soluble salts, which offer the following advantages:

(1) The contact mass is easily regenerated by placing it in water, when the soluble salts dissolve, leaving the platinum. It is therefore not of such great importance to have the gases exhaustively purified, since the catalyst is easily made up again.

(2) The crusts of calcined salt are very porous, and offer much less resistance to the passage of the gases than the compact masses, such as tightly packed platinized asbestos, formerly used.

(3) The catalytic activity of the new mass is so high that, whereas in the old plants asbestos containing 8% to 10% of platinum was required, the new contact mass may contain as little as 0.1% Pt.

In the original patent,⁴ the preparation of the catalyst is described as follows: Soluble salts of the alkalis, earths, or alkaline earths, and of the metals are dissolved in water, and then mixed with a solution of the platinum salt. The mixed solution is then evaporated, and the resulting salt crusts dried and broken up to a uniform granular size. The powder resulting from the

1. D. R. P. 22118, 1883; abst. Wag. Jahr. 1883, **29**, 269.

2. J. S. C. I. 1903, **22**, 348; abst. Jahr. Chem. 1903, **56**, 347.

3. U. S. P. 636924, 1899.

4. U. S. P. 636925, 1899.

breaking up is re-dissolved in water and treated as before until all the material has been converted into granules of the appropriate size. This material can be filled directly into the contact chambers. The separation of the finely divided platinum on the surface of the supporting salt occurs on heating, i. e., on starting the process.

As salts suitable for supports, only those are available which remain unchanged during the contact process, i. e., such as contain stable sulfates or an acid, for instance phosphoric, which is stronger at a low red-heat than the sulfuric acid (sulfur trioxide) formed in the contact process. Other salts, such as chlorides and carbonates, will be decomposed at the commencement of the heating, and as this leads to an alteration of structure and injury to the firm cohesion of the individual granules, these salts cannot be used. As an example of the preparation of the catalyst, the following procedure is cited: 100 lbs. each of potassium, magnesium and aluminium sulfates, are dissolved in the smallest quantity of water, and 10 lbs. of concentrated aqueous platinum chloride added. The mixture is evaporated, dried, and granulated. The platinum is in a condition of maximum activity, and appears to be effective in the interior of the pieces not less than on the surface, no doubt on account of the great porosity due to the driving off of the water of crystallization.

If the surface of the contact mass becomes covered with impenetrable layers of dust from the gases—thus diminishing the efficiency of the catalyst—it is only necessary to revivify the material by dissolving it in water, and evaporating the solution thus obtained. After the soluble salts have been removed by water the dust may be separated from the platinum by boiling with concentrated hydrochloric acid.

The preparation of the catalyst may be carried out in the contact apparatus itself.¹ A blower forces air through a series of pipes heated in a furnace, and the air, at about 200°, passes into the bottom compartment of a cylinder, below a grating on which is spread a thin layer of, say, anhydrous magnesium sulfate, covered with crystals of the same salt moistened with platinum chloride solution, or mixed with platinum powder, more of the

J. A. G. für Zinkindustrie, vorm. W. Grillo and M. Schroeder, E. P. 10412, 1901; abst. J. S. C. I. 1902, **21**, 344. Cf. E. P. 25158, 1898.

moist salt being added successively as each layer dries, until the compartment is sufficiently charged. Another compartment is then bolted or secured on, and the process repeated, continuing until the desired number of compartments have been charged. When thoroughly dried the material is ready for the production of sulfur trioxide. To increase the formation of blow-holes in the mass, sugar or gum may be added, the carbon of which subsequently burns away.

In a later patent¹ an apparatus for carrying out the contact process with the porous catalytic material is described. The purified gases before passing to the retorts containing the contact mass stream through tubes exposed outside to the hot burner gases, and so acquire the requisite amount of heat. The apparatus is shown in Figs. 101-103. The double row of pyrites burners *A*, having a common rear-wall *a*, are provided with transverse walls *b*, extending almost to the roof-arch, and supporting the pipes conveying the purified gases to the contact retorts *c*, which may be enclosed in a suitable furnace *B*. The pipes may be of iron, *D*, arranged parallel to the dividing-wall. The cooled gases from the main *C'* enter the purifier *D'*, and in their cooled condition pass into the pipe *B*, from which they are forced or drawn by a blower or exhauster through the two branches of *D*. This subdivision is made because of possible irregularities of firing on the two sides of the furnace-bench. In passing through the branches of *D* the purified gases absorb heat from the unpurified gases passing outside the pipes, and then pass into a main *E*, covered with asbestos, leading to the contact retorts *c*.

In the modification shown in Fig. 102 the unpurified furnace gas passes from the flue *P* into a series of tubes *h* in the same manner as in the fire-box of a locomotive, these tubes being carried by end-plates *i*, forming with the walls of the structure *G* an enclosed system, into which leads the inlet-pipe *m*, conveying the purified gases under pressure from the purifier. An exit pipe *n* conveys the purified gases after they have been reheated by contact with the exterior walls of the tubes *h* to the contact retorts, while the unpurified gases after giving up the corresponding

1. M. Schroeder, assignor to N. J. Zinc Co., U. S. P. 742502, 1903; abst. J. S. C. I. 1903, **22**, 1243; Chem. Zts. 1904, **3**, 244, 291; J. A. C. S. 1904, **26R**, 233; Mon. Sci. 1904, **61**, 31.

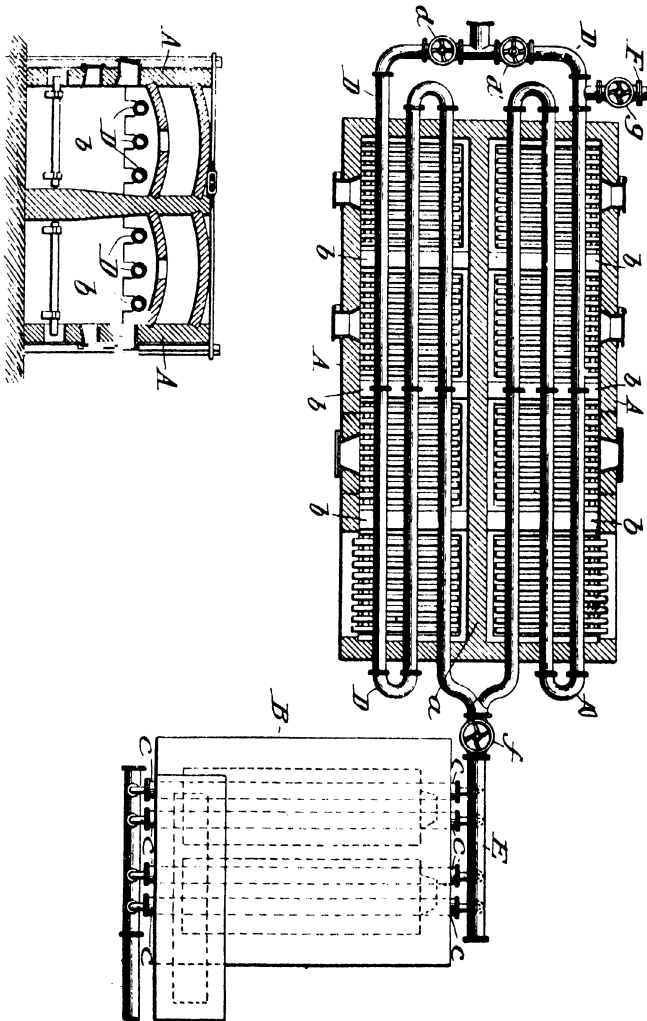


FIG. 101.—THE SCHROEDER-GRILLO PROCESS OF SO_2 MANUFACTURE

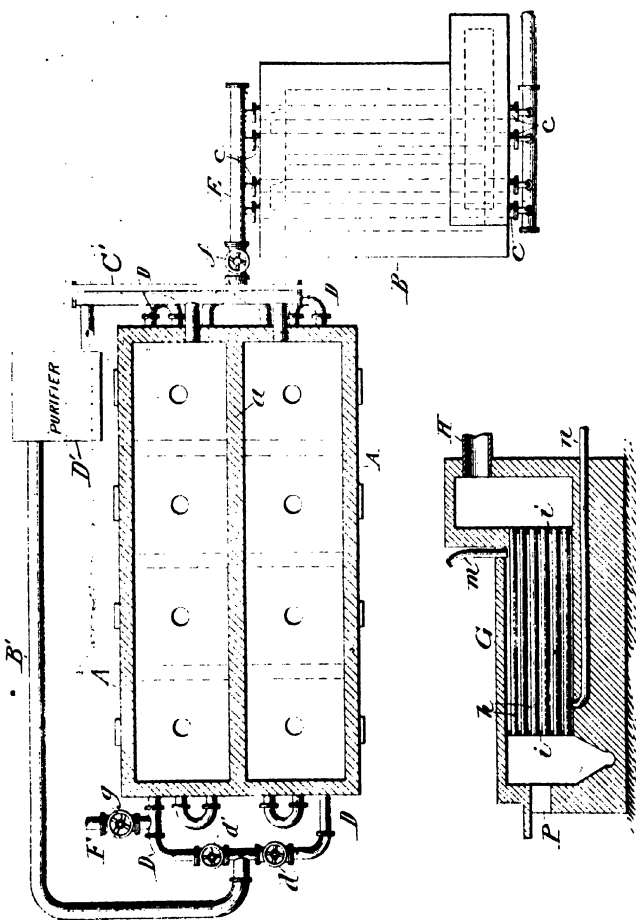


FIG. 102.—THE SCHROEDER-GRILLO PROCESS OF SO_2 MANUFACTURE

quantity of heat to the purified gases pass on through the flue *H* to the purifier.

In the apparatus shown in Fig. 103 the unpurified furnace gases pass upwards through the vertical shaft *I* on their way to the purifier and give up their heat to the purified gases which, entering under pressure through the pipe *p*, pass into the vertical conduit *r*, from which in a highly heated condition they proceed to the contact retorts. The shaft *I* may, if desired, contain a loose filling of firebrick or other heat-storing material, and a supplementary furnace *S* may also be used to supply a further amount of heat.

A subsequent patent¹ describes the arrangement of the contact apparatus with gas-mixers and preheaters. In Fig. 104 the receptacle containing the contact mass *g* is divided into a number of separate compartments by partitions *a*, with openings *b*, through which the gases pass to the exit pipe *h*. A grating *c* is placed above each partition, on which the contact mass is placed. The temperatures are measured in the various compartments by pyrometers *k*. In starting up the reaction, a fire may be put upon the grate *f*; it is not necessary to preheat the gases above 260°–280° before entering the contact mass. The vessel containing the contact mass may be divided up into separate compartments, it being in all cases immaterial whether the gases pass up or down through the contact mass.

As regards the initial purification of the gases, it is stated² that towers of large diameter filled with coke and sprayed with sulfuric acid have in most cases been found sufficient. In the United States the asbestos filters of G. Stone³ are also used. The question of impurities has been discussed by this inventor,⁴ who points out that in cases where sulfur or blende are used instead of pyrites, the problem is different from that dealt with by the Badische Co., since arsenic is not usually present in appreciable amounts. With blende, the main impurities are fluorine, which forms a layer of silica on the contact mass, owing to the presence of silicon fluoride in the gases, and chlorine, either free

1. M. Schroeder, assignor to N. J. Zinc Co., U. S. P. 793543, 1905, abst. J. A. C. S. 1906, **28R**, 80; Mon. Sci. 1906, **65**, 19.

2. J. S. C. I. 1903, **22**, 348; abst. Jahr. Chem. 1903, **56**, 347.

3. U. S. P. 711187; abst. Chem. Zts. 1903, **2**, 158, 274; Chem. Ztg. 1902, **26**, 1061.

4. J. S. C. I. 1903, **22**, 350; abst. Jahr. Chem. 1903, **56**, 347.

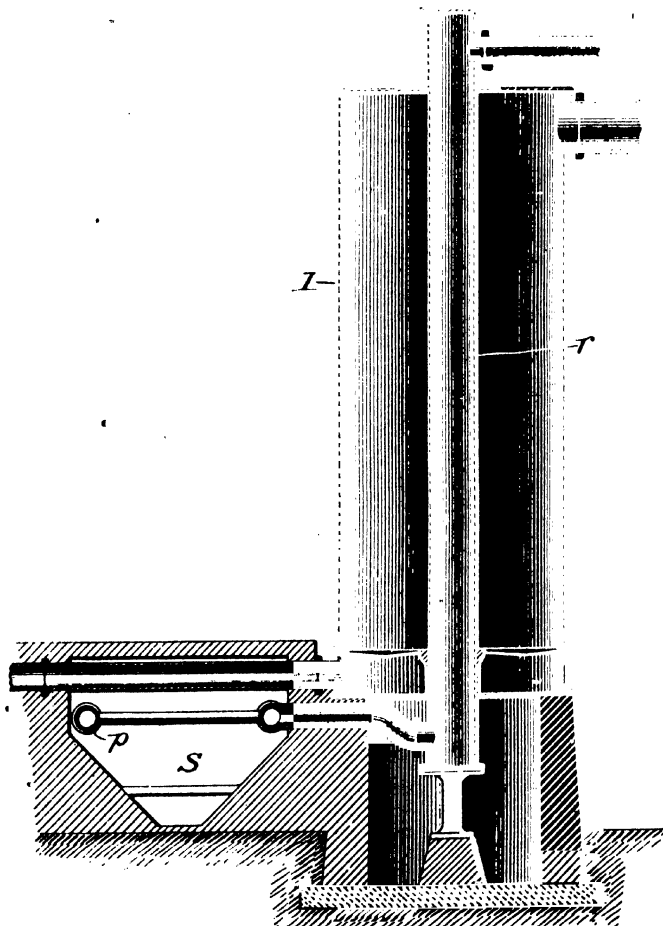


FIG. 103.—SCHROEDER-GRILLO PROCESS OF SULFURIC ANHYDRIDE MANUFACTURE

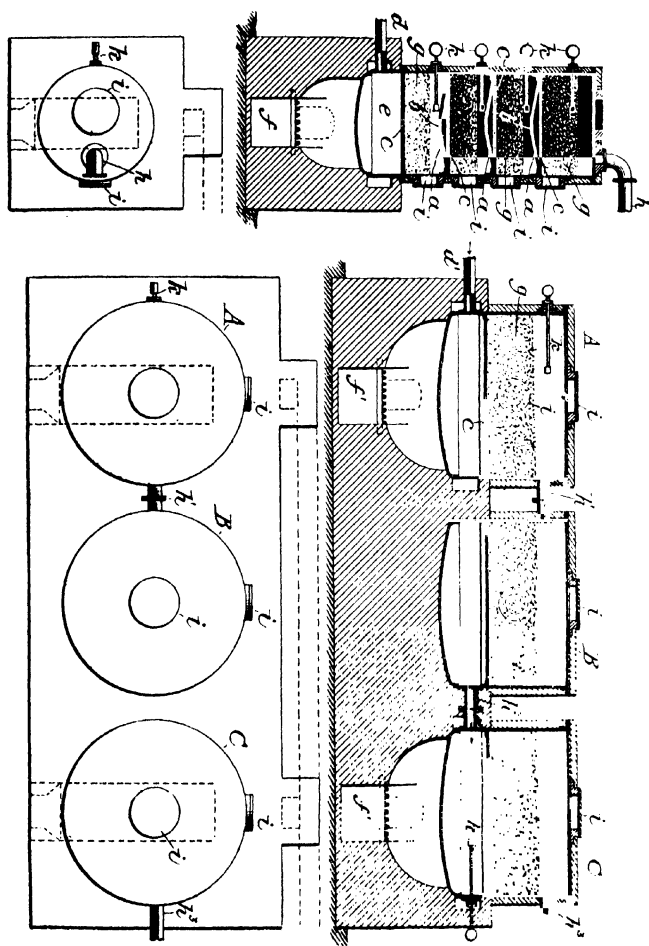


FIG. 104.—THE SCHROEDER-GRILLO SULFURIC ANHYDRIDE PROCESS

or as hydrochloric acid.* The latter impurities have only a temporary effect, which disappears when pure gases are used. In regenerating the contact masses they are spread on a cement floor, sprinkled with a mixture of dilute nitric and hydrochloric acids containing sugar, mixed to a stiff paste, allowed to stand a couple of days, heated to drive off water and excess of acid, cooled and crushed, and are then ready for use.

In the Schroeder plants actually used, Stone states they consist of the following parts:

1. A dust-catcher next to the burners.
2. A cooler, in which the gases are reduced to the atmospheric temperature.
3. Scrubbers or washing towers of different kinds, depending on the character of the gas, which also serve to dry the latter.
4. Filters, which are the most important part of the purifying system, and remove most of the arsenic, selenium, and other volatile impurities.
5. Preheaters, through which the gases are forced from the filters by a positive blower, and heated to 300°–400°.
6. The converters.
7. The coolers, in which the converted gas is cooled to 50°.
8. The absorbing tanks and towers, in which the gas is brought in contact with a large surface of moderately cool acid. Acid up to 40% SO_3 may be made directly in the absorbers.

The average conversion is stated to be about 96%, which is nearly independent of the content of SO_2 in the burner gases, and there is very little time lost in stoppages.

An account of the experimental investigations of the process has been given by C. Reese,¹ the following being the main results:

1. The purified burner gas may be saturated with moisture before passing to the converters without affecting the conversion in any way.
 2. Carbon dioxide and monoxide have no deleterious effect on the conversion.
 3. The presence of free sulfur in the gas has no deleterious effect.
 4. Hydrochloric acid, chlorine, silicon tetrafluoride, arsenic
1. J. S. C. I. 1903, **22**, 351; abst. Jahr. Chem. 1903, **56**, 347.

and lead are prejudicial to the process, and act apparently in two ways: (a) by their mere presence in the gas, hydrochloric acid, chlorine and silicon tetrafluoride; (b) by affecting the activity of the contact mass, lead, arsenic.

The effect with the substances of class (a) is temporary, that of class (b) permanent. The fine mist of sulfuric acid contained in imperfectly filtered gases carries with it arsenic, lead sulfate, sulfur and selenium. If these are removed by filtration, so that the gas is optically pure, contact mass lasts indefinitely.

According to Reese, the optimum temperature of operation is 425° , but there is little variation in the results obtained between 400° and 435° . The reaction commences at 330° – 340° .

An account of the Schroeder plant erected at the U. S. Naval Proving Ground at Indian Head has been given by G. Patterson and L. Cheney.¹ The plant was erected in 1907, and designed by the New Jersey Zinc Co., which controls the Schroeder patents in the United States. More recently it has used Louisiana brimstone.

A Tromblee and Paull burner (p. 1054), consuming 6000 lbs. S per day is used, and the gases passed through a brick dust-catcher of the usual type. The exit from this has a temperature of 230° , and enters the purification system. This is made up as follows:

First the gases pass through 250 ft. of horizontal lead pipe arranged in tiers in a wooden rack, where a small quantity of weak sulfuric acid is deposited. The pipe connects with a lead-lined box filled with coke, where more acid is condensed. From this the gas passes to two wet scrubbers in tandem, each consisting of a vertical lead cylinder with a conical top, about 4 ft. high, a lead pot provided with lead cooling coils for water, and an air-lift for constantly circulating a stream of sulfuric acid from the pot to the scrubber, which is divided horizontally by perforated diaphragms. The acid thoroughly washes and dries the gas, and flows out through a trapped pipe to the pot, holding 2500 lbs. of acid, which is constantly strengthened to gravity 1.75 by addition of strong acid. The excess acid formed is collected in an egg and

1. Eighth Intl. Cong. Appl. Chem. 1912, **2**, 215. J. Ind. Eng. Chem. 1912, **4**, 723; abst. J. S. C. I. 1912, **31**, 1028. See also R. Curtis, Chem. Trade J. 1919, **64**, 409; abst. C. A. 1919, **13**, 1745; J. S. C. I. 1919, **38**, 369-R.

can be forced by air pressure to the weak acid supply used in the absorption system.

From the scrubbers the gas passes to a second lead-lined box exactly like the first one, and then to a pair of dry filters in parallel, each consisting of three superimposed lead-lined iron trays luted together, each tray containing a mat of dry asbestos fiber supporting a quantity of slag wool. A reserve set of filters is provided. The charge for the two filters is 30 lbs. asbestos and 400 lbs. slag wool. Beyond this point the gas is conducted through cast or wrought iron entirely.

The filter house contains a positive pressure blower, with a suction of 1.5" mercury before, and a pressure of 0.75" after. The gas sampling tube is placed before the blower. The gas next passes to the preheaters, consisting of a series of vertical U-tubes and headers heated in a furnace with soft coal to an initial temperature of 380°.

The converter is erected close to the preheater, and comprises a vertical cast-iron cylinder 6 ft. diameter and 8½ ft. high, composed of 5 horizontal sections, each containing a wire mesh tray for supporting the contact mass, and a baffle to spread the gas.

The contact mass consists of anhydrous magnesium sulfate containing 0.2% platinum, a total of 5900 lbs. of mass, spread in coarse granules on the trays to a depth of 14–16 in., leaving 6 in. spaces, being used. The gas enters at the bottom and leaves at the top, the temperature being controlled by pyrometers.

From the converter the gas passes through 180 ft. of iron pipe to the absorbers, consisting of a tower absorber, an acid cooling pipe, a weak acid mixer and reservoir, a head tank for strong acid, an acid pump, and collecting tank. The tower is a vertical cast iron cylinder 15½ ft. high resting on a cast iron base, the top being covered with a perforated plate from the center of which rises the gas exit pipe. The tower is lined with acid tile and packed with quartz. The gas enters at one side near the bottom, a constant stream of acid is pumped to the top plate, percolates through the packing, and leaves at the bottom to the cooling pipe. This is a horizontal water cooled U-tube, one leg of which carries an overflow pipe connecting with the pump and

collector. The acid supplied to the top of the tower is kept at 70° and a strength of 99.5% H_2SO_4 . The strength of the acid leaving the tower is reduced by the constant addition of a small stream of 75% H_2SO_4 just before entering the cooler.

The reservoir for this weak acid, the mixer, and the strong acid head tank, are mounted on a platform in the center of the building at a sufficient height to give a flow by gravity. The reservoir is an open lead-lined box holding 1000 gallons, the mixer being a lead pot provided with lead cooling coils and a special mixing pipe, consisting of two heavy $\frac{3}{4}$ " lead pipes set at a 30° angle and held together by a heavy lead sheath burnt on to a short length of $1\frac{1}{2}$ " lead pipe. One of the $\frac{3}{4}$ " pipes carries strong acid from the head tank and the other cold water from the mains. The $1\frac{1}{2}$ " pipe carries the mixture to the pot. The head tank has a capacity of 18,000 lbs. strong acid.

The conversions are 95%-95.5%, the average consumption of coal being 21.8 lbs. per 100 lbs. SO_3 made. An entrance gas of 6.5%-7% SO_2 is used, the average production being a little more than 6 tons of acid per day.

During the war the Schroeder process was extensively used, with very satisfactory results. The general arrangement of apparatus was in most cases similar to that described by Patterson and Cheney, but on a much larger scale. Some of the plants erected and operated in Great Britain, at Queen's Ferry, near Chester, and at Gretna, in Scotland, were the largest ever erected, and operated smoothly and economically. An account of the operations in these factories is given in two Government Documents entitled "Costs and Efficiencies for H. M. Factories controlled by the Factories Branch, Department of Explosives Supply," 1919. These reports also contain valuable information as to the concentration of acid. Comparisons with Canadian and American practice are recorded in the documents, from which it appears that on the whole the British plants were more efficient in operation.¹

A few details of the operation of a large Schroeder-Grillo plant are given below as a guide to what may be expected in similar plants, although the exact results naturally may vary somewhat with the size of the plant. The plant was producing

1. See J. S. C. I. 1919, **38**, 224; R. Curtis, J. S. C. I. 1919, **38**, 369-R.

about 150 tons of sulfur trioxide per week, sulfur being burnt.¹

It was found that about 3% of the sulfur was burnt to SO_3 in the hand-operated burners. Of the water drawn into the burners, the cooler required 4%, the first two filters 38% and the scrubbers 44%, about 5% leaving the scrubbers. Of the SO_3 formed in the burners 1.9% is removed by the coolers and filters, 0.8% in the scrubbers, and 0.23% passes on. In the absorption system, consisting of six towers, containing acid of strengths given, the following amounts of SO_3 were removed:

| Tower No. | Acid in Tower % H_2SO_4 | % Absorption in Tower |
|-----------|--|-----------------------|
| 1 | 15-18 free SO_3 | 67 |
| 2 | 99 | 27.6 |
| 3 | 98.1 | 5.4 |
| 4 | 15-18 free SO_3 | 73.5 |
| 5 | 99 | 21.1 |
| 6 | 98.1 | 5.4 |

The best temperature of absorption was found to be 75°-85° for the inlet gases. The acid in No. 3 tank (98%) should be kept below 40°, as a rise to 45° causes a marked drop in efficiency. The composition of the burner gas must remain as constant as possible, as fluctuations cause lower efficiencies, probably because of the changes of temperature in the contact mass.

Grillo Process at Queen's Ferry. From the exhaustive report of V. Gloag and J. Riley, the following data is reproduced in respect to the installation of the system in England (see p. 1161). The SO_3 required to replace the losses in the working of the acid cycle, is produced at Queen's Ferry by both the Grillo and by the Mannheim Processes, the latter being erected first, but it has only served in a subsidiary capacity since the erection of the Grillo plant.

The process, in brief, comprizes the ignition of sulfur in special burners, giving a mixture mainly of air and SO_2 , which is cooled and dried, further air being admitted to adjust the partial pressure of the SO_2 . The gas is then heated to the desired temperature by a regenerative method, and passed through converters, the SO_3 leaving the converters being cooled and absorbed

1. Attention is directed to Experimental Reports Nos. 20, 23, 24, 26, 27, 52, 56, 65, 103, 106, 107, 109, H. M. Factory, Gretna (Dornock), which discuss various phases of the operation and control of a successful Grillo Schroeder installation.

in towers by sulfuric acid, yielding a final acid of either about 98.6% H_2SO_4 , or 20% oleum.

The lay-out consists of ten independent units, which operate in three systems, and two sub-systems, as follows:

(a) A single unit, on water feed and absolutely isolated from the remaining units, produces an oleum absolutely free from arsenic, which is utilized in the scrubbing towers of all units for the drying of the SO_2 -air mixture.

(b) Three units are connected to the nitrocellulose acids cycle, and fed with acid from the Gilchrist concentrators.

(c) Six units run in connection with the TNT acids cycle, being fed with feed acid from the Gaillard towers. This system is divided into the two sub-systems, (i) four units producing 98.6% H_2SO_4 , and (ii) two units producing 20% oleum.

Sulfur Stores. Of the two sulfur stores, the first (250' x 63' x 29' high) feeding six of the units, and the other (215' x 58' x 29' high) serving the needs of the other four units. The stores are of corrugated iron, the walls being inclined on the "angle of repose" system, to render possible the utilization of the full capacity of the store, without any drossing of the sulfur. The sulfur is discharged from trucks into a bin, from which it is transferred by a rubber belt-conveyer, running along the entire length of the top of the building. An automatic tippler enables the sulfur to be discharged from the belt to any desired part of the store. The full capacities of both buildings are 7000 and 6500 tons respectively. The sulfur is weighed out in this building in scoops ready for charging, (see Figs. 88, 89, p. 1066), the maximum charge for one scoop being 40 lbs. The full scoops are trucked to the burners by the burner girls as illustrated.

Sulfur Burners, of which twelve comprize a unit (see Fig. 89), consist of cast iron trays, each 7' 2" long, 3' 5½" wide and 5" deep. The sulfur is charged into the pan through a cast iron charging door, where, in the burner it is partly burned and partly volatilized, the products being drawn through an upcast, back over the arch above the cast iron tray, then passing up through a checker-work chamber to the main burner flue to the 12 burners. This leads the gases to the end farthest from the heater-cooler where they pass through a cross-connecting flue into a back-flue

which conducts the gases directly to the large heater-cooler.

In order to regulate the draught on the separator burners and thus control the temperature, each burner is connected to the main back-flue by a small short-circuiting cross flue, 9" x 9". The air necessary for the complete combustion of the sulfur is admitted in three places:

- (a) Through a slot in the charging door of the burner.
- (b) In the rear of the burner, through a 5" square opening leading from the hot air flue situated in the main body of the burner, immediately below the back flue.
- (c) Through a slide in the front of the burner, immediately above the burner door. This air mixes with the gases immediately before their admittance to the checker-work combustion chamber.

The normal charge of 75 lbs. per burner per hour, or 9.64 long tons per unit per 24 hours, gives a maximum efficiency. The burners have been proven experimentally capable of burning 100 lbs. per hour.

Operation of the Burners. Two burners are charged each ten minutes. Thus Nos. 1 and 7 are charged on the hour, Nos. 2 and 8 at ten minutes after the hour, and so on, each burner being charged hourly, and the draught regulated so as to extend the burning of the charge throughout the full period. The relation between the control of the burners and the efficiency of the converters is very close, a discontinuous method of charging inevitably resulting in fluctuation in the composition of the burner gases, but with care the variation in gas composition can be reduced to less than 0.4% at the converters. The gas composition stipulated at the entrance to the converters is $4.8 \pm 0.2\%$ SO_2 .

With S containing 2% ash, it is necessary to clean out the burners every three or four days. After cleaning, the sulfur burns off much more rapidly, thus increasing the danger of sublimation, particularly when working to a high percentage of SO_2 in the burner gases. To overcome this tendency, and reduce the rate of combustion, about $\frac{1}{2}$ "-1" of ash is always retained in the burners. To work regeneratively on 75-lb. charges, a temperature of 800° is required in the flue entering the heater-cooler. This is easily guaranteed by maintaining a gas from the burners with about

an eleven to about twelve per cent. sulfur dioxide content.

Heater-Cooler. The burner gases pass to the heater-cooler through a short lagged flue, from which an 18" dampered connection permits the by-passing of all gas direct to the stack, in case of necessity. The heater-cooler consists of a brick chamber 23' 6" long x 18' wide, divided into two compartments containing altogether 6 rows of 5" U-pipes, 8 in a row. The hot burner gases circulate round these and heat transference takes place to the pure 5% SO₂ gas passing through the U-pipes. These gases enter the heater-cooler at about 800°, and issue at about 290°.

Experience has indicated that the total cross-section of the U-pipes is too small, with the result that, when high charges are being worked, the resistance to the flow of gases is unworkably high, as shown by the following table:

| | 60 lb. | 80 lb. | 100 lb. |
|-------------------------|-------------|-----------|------------|
| Pressure entering H. C. | 41.5" W. G. | 78" W. G. | 102" W. G. |
| Pressure leaving H. C. | 19.7" | 38" | 51.2" |

The only satisfactory remedy appears to increase the number of U-pipes, and so increase the cross-section, and thereby diminish the resistance. Constructed as above outlined, charges greater than 75 lbs. per burner-hour would only be rendered possible by permitting the SO₂ content of the gas entering the converters to exceed 5%.

SO₂ Coolers. These reduce the gases leaving the heater-cooler to atmospheric temperature, the coolers as a whole consisting of two separate cooling systems of lead cooling pipes arranged in parallel, and constructed right and left handed respectively. Each system consists of twenty 20" diameter vertical lead pipes connected by headers, the total cooling surface being 4200 sq. ft. Cooling is accomplished by water run over the coolers from sprinklers or distributors, the lower bends being totally immersed in water. The gases enter the coolers at 290°, and leave it at a maximum temperature of 20°.

The gases enter each cooler through two cast-iron pipes 26" diameter, lined with 2" acid-proof joggle-jointed tiles. A 1" drain-pipe from the bottom of each lower bend leads the acid which condenses into a lead catch-pit, from which it is elevated to the weak acid storage tanks, for despatch with the weak

scrubber sulfuric acid directly to the concentrating plant.

Purification System consists of 5 coke-packed filters and 3 similar scrubbing towers. The cool gases first pass through two filters, passing from top to bottom of the first, and in the reverse direction in the second. The direction of flow in the first filter ensures that any sublimed sulfur will be trapped on top of the coke bed, from which it can be cleared by raking.

The gas then passes through the weak scrubber over which 55%-60% acid is circulated to absorb the halogens. Between the first and second scrubbers, the necessary air is admitted to dilute the gas down to the necessary 5% SO_2 content. It then passes through the remaining scrubbers over which 75%-80% acid and 93%-95% acid respectively is circulated, and finally through the last three filters, passing in each case from bottom to top. Where the air is introduced as described above between the first and second scrubbers, there is an enormous decrease in trouble from mist.

Filters. These are all 30' x 12' x 10', made of 8-lb. lead, and packed with coke, resting on a brick grid to within 18"-20" of the top. The size of the individual pieces is reduced in steps from 4" to $\frac{1}{4}$ ". An arrangement is fitted to permit of the spraying of the acid into the scrubber if necessary, the precipitated acid being drained off to the weak acid storage tanks. All connections between filters and scrubbers are 30" diameter.

Scrubbers are 20' x 12' x 12', lined with acid-proof bricks and packed with coke resting on a brick-work grid. Acid of the strengths previously mentioned are circulated by means of a 10" Rees Roturbo pump, shifting approximately 20 tons per hour. The circulation tanks are 10' x 2' 6" x 3' 6" and the feed tanks 7' x 4' 6" x 3' 6", both being of 12-lb. lead. The acid is fed to each tower from the feed tanks through 72 luted distributors, and after percolating through the packing, is run off at the base through a seal, cooler and settling tank into the circulation tank. The necessary fresh acid is fed to the scrubbers through the cooler on No. 3 tower. On 75-lb. charges, the total time of passage of the gases through the scrubbing system is 2.73 minutes.

The following generalities have been found to apply:

(a) The packing of the filters should approximate to the following: 24" of 4"-6" coke, 12" of 4", 12" of 2", 4" of 1", and

48" of $1/2''-1/16''$ coke, the latter being free from dust.

(b) With a SO_2 content of 12% in the burner gases and air admitted after the first scrubbing tower, the quantity of mist eliminated after the purification system has been much greater than when this air was admitted at the SO_2 coolers.

(c) The weak scrubber acid must be maintained in the region of 55% H_2SO_4 in order to effectively absorb the halogens, but in order to prevent the weak scrubber acid from becoming saturated and stale, a suitable quantity of weak acid is run off daily, 30 cu. ft. of fresh oleum added to each strong acid scrubbing tower, the weak scrubber being kept at 55% by the addition of 600 lbs. water.

(d) Strong mists are deposited more readily than weak mists, the tendency being to deposit the $\text{SO}_3\text{H}_2\text{O}$ and $\text{SO}_32\text{H}_2\text{O}$ hydrates.

Pressure Equalizer. The gases pass from the purification system through a 30" mild steel pipe to the pressure equalizer, which is a mild steel shell five feet in diameter and three feet deep, fitted with 3 diaphragm plates with $1/2''$ holes, $3/4''$ from center to center. These having proven insufficient to reduce the vibration on No. 5 filter, all pressure equalizers were re-fitted with 6 plates each, lead covered, with the exception of one-fourth of its area.

The pressure equalizer functionates as a mist catcher, and between 20 and 50 lbs. acid are deposited per day, the amount varying with the atmospheric humidity. After leaving the pressure equalizer, the gases pass through a 2' diameter mild steel pipe to the Roots blower, which is capable of handling 27 cu. ft. of gas per revolution, which at 150 r. p. m. is equivalent to $6\frac{1}{2}$ million cu. ft. per day. The blower is driven by a 60 h.p. motor. A 100 h. p. blower is not recommended, on account of the serious resistance offered by the heater-cooler before mentioned.

Grease Catcher. The gases pass to this from the blower through an 18" pipe. The grease catcher is a mild steel shell, 8' diameter by 30' long, packed with graded coke. The gases enter from below, passing through a grid and thence on through the coke, thus precipitating the final traces of mist. The acid precipitated is run off through the acid seal.

Heat Exchangers. The gases are delivered from the grease catcher through a 15" diameter pipe into two 10" diameter pipes

leading to two heat exchangers, where they are heated at the expense of the gases leaving the converters.

Each heat exchanger is a mild steel shell, 10' long x 4' 2" inside diameter. The gases pass through a series of 2½" steel tubes 8' 4" long (104 in all) which are fitted inside the shell, being heated from the gases of the converter which pass outside the tubes, being given the necessary turbulence by means of two baffle-plates. The heat exchangers are considered very efficient, 460 C. H. U.'s per hour being exchanged per sq. ft of surface.

The gases leave the heat exchangers by 10" exits, jointing into a single 15" pipe, and pass to the heater cooler as previously described, for further heating prior to admission to the converters.

Pre-heaters. If the unit is not running regeneratively, i. e., if the charge is below 60 lbs., the gases require heat to supplement that gained in the heat exchangers and heater-cooler. This is supplied by the pre-heaters, of which there are two per unit.

Each pre-heater is coal-fired in two fire-grates, 4' 6" x 3' 6", the burned gases passing into a common chamber, 16' 6" wide x 8' 2½" long x 2' 4" high, and thence into two heating chambers, each 20' 6" long x 6' 9" wide x 13' 7½" high, and containing 24 cast-iron U-pipes in series, through which pass the gases from the heat exchangers. The waste gases pass through 4 flues 2' square to the 4' x 65' stack.

Converters. Two converters per unit are provided, each containing 10,000 lbs. of mass with a 0.3% platinum content. For each unit there are, therefore, 20,000 lbs. mass, or 60 lbs. platinum. Each converter consists of an outer shell 7' 4" in diameter by 12' 8" high, closed at the bottom by a dished plate, fitted with a 10" diameter outlet.

The inner shell is arranged to receive four separate layers of contact mass, each weighing 2500 lbs. and spaced at intervals of 2' 11½". The mass is carried on 3/16" perforated plates, and 8½" below each plate is attached a cast iron baffle plate of 5' 8" diameter, thus leaving an annular space of 5" between the edge of the plate and the sides of the inner shell. The baffles serve to divert the gases after each contact, to the walls of the shell, thus securing the desirable heat exchange between the inner and outer gases.

The hot dry SO₂ air mixture enters the outer shell tangentially,

at the base, through 10" diam. inlet pipes and is compelled by baffles to circulate spirally in the space between the two shells, being heated at the expense of the gases inside the inner shell. Having arrived at the top of the inner shell, the gases pass downwards first through a layer of unplatinized mass, and then in turn being heated on account of the heat conversion as each contact mass is passed through and cooled as the corresponding baffle plate compels circulation along the sides of the shell. Finally the gases pass through the 10" outlet to the heat exchangers as already described and thence to the SO_3 coolers.

Conversion. The essential condition for good conversion, i. e., 96%–97%, are briefly:

(a) Careful separation of burners and supplementary inlet to obtain a steady composition ($1.8 \pm 0.2\%$ SO_2) of the gas entering the converters.

(b) Efficiency in the purification system.

(c) The maintenance of low temperatures in the converters, no temperature to exceed 480° .

(d) The exit temperature of the gases leaving the converters should be about 410° .

(e) All temperatures should be kept steady. The temperature at which conversion commences is a function of the velocity of the gases, as it is shown in the following table:

| Sulfur Charge | Velocity of Gases Ft. per Sec. | Temp. at which Conversion Starts |
|---------------|-----------------------------------|-------------------------------------|
| 75 lbs. | 4.0 | 360–370 |
| 70 lbs. | 8.0 | 370–380 |
| 80 lbs. | 9.2 | 390–400 |

The converter temperature must be carefully watched, so that an even distribution of load is obtained, the maximum temperature at any point being 480° and the exit temperature within 10° of 410° . Temporary poisoning of the contact mass—such as due to the halogens—has the same effect as increasing the velocity of the gases, in that a higher temperature is required to start conversion, if it can be raised quickly, temporary poisoning can be overcome, otherwise poison must be removed by roasting the mass for about 4 hours with air at 450° .

SO_3 Coolers. The gases pass from the heat exchangers, through 10" mild steel pipes, to two separate SO_3 coolers, each of which

consists of 8 sets of horizontal 6" U-pipes in parallel, arranged vertically one above the other, the total length of each U-pipe being 60 ft., the cooling surface for each SO_3 cooler is thus 840 sq. ft. or 1680 sq. ft. for each unit, neglecting the 10" headers and branches. The gases pass from the coolers to the absorption system. The SO_3 coolers can be operated either as air coolers or water coolers. Air cooling is preferable, cooling with cold water causing local cooling of the SO_3 and leading to polymerization and hence bad absorption. The difficulties to be encountered are therefore:

(a) In summer high charges necessitate water cooling, resulting in poor absorption, the only remedy being the increase of cooling surface.

(b) In winter if low charges become necessary, the danger of freezing the SO_3 , even with air cooling, necessitates a substantial reduction in the existing cooling surface.

Absorption System. This is arranged in two parallel series of 3 towers of mild steel towers, 6' in diam. and 24' high, lined with acid-proof tile and packed with quartz, carried on an iron grid. The gases pass through each tower from bottom to top, and after leaving the last tower, make their exit to the atmosphere. Each tower is provided with a circulating acid tank, lined with acid-proof brick. The acid is circulated round the towers by means of Rees Roturbo centrifugal pumps, throwing the necessary tonnage to secure complete absorption.

(a) *90.5% Units.* Feed acid from the concentrator is fed into the acid leaving the absorption towers at such a rate as to maintain a constant strength of 98.5% in the circulating tanks, the acid passing down all the towers in parallel, after leaving which, it passes through a common 6" cast iron cooler back to circulation, the material being continuously run off to a stock tank and pumped to storage.

(b) *Oleum.* The circulation is worked in two systems, one with 98.5% acid and the other with 20%-21% oleum, a cast iron cooler being fitted on the first and a mild steel cooler on the second, the feed acid being so regulated as to ensure a constant run-off of 20%-21% oleum.

Acid Coolers. All units are provided with cast iron coolers for the 98.5% sulfuric acid. These are approximately 600' long

x 6" internal diam. The oleum units are provided with additional oleum coolers of 5" steel pipe 500' long.

Preparation of Contact Mass for Grillo Plant. The magnesium sulfate crystals are first calcined in flat iron pans, 5' x 2' 9" x 3" deep, giving a cake after baking, containing about 14% moisture. This is passed through a Sturtevant crusher, set for the finest product, and ground to dust (1st dust) in a Devil disintegrator, mixed with water on a hot pan of the same dimensions as the first, and rebaked or recalcined. The second cake is passed through a Sturtevant crusher, set for the coarsest product, and then run through a rotating trommel screen and graded as follows: (a) Dust under $\frac{1}{4}$ "; (b) Mass from $\frac{1}{4}$ " to $\frac{1}{2}$ "; (c) Oversize over $\frac{1}{2}$ ". The mass (b) is then stored ready for platining while grades (a) and (c) are passed through the disintegrator, for the formation of dust for rebaking.

The finished mass contains slightly over 9% of water, and should be hard, resembling pumice-stone in its tenacity, and leaving a vitreous fracture. A good test for the hardness of the mass is obtained by rubbing two pieces together. Good mass will resist the friction and pressure, only giving a little surface dust and tending to become polished. It is extremely important that the mass should not be friable, as this will result in disintegration when the mass is introduced into the converter, which will probably lead to loss of platinum, as well as causing increased resistance to the passage of the gases through the converters.

Production of First Cake. The following summarizes the essentials for the production of a satisfactory cake:

(a) The purest crystals only should be used, otherwise a porous cake results.

(b) As soon as the contents of the pan have become solid, it must be frequently rubbed over to secure a compact mass.

(c) The normal time of baking is about 7 hours, but prolonged heating does not effect the cake adversely.

(d) The normal charge per pan is 2 cwts.

(e) The dust must be as fine as possible, smooth to the touch, and free from un-reduced grits.

Production of Second Cake:

(a) This should be made from equal proportions of the first

and second dust, which should be uniformly and thoroughly mixed.

(b) The charge per pan equals 140 lbs. of dust mixed into a thick cream with about $6\frac{1}{2}$ gals. water. This gives a cake 1.1"–1.3" thick.

(c) The mixing with rakes must be very thorough.

(d) The initial temperature of the pan must be such as to cause the mixture to boil freely but not vigorously. If this condition is secured, and the mixing is carried out properly, the cake dries out quickly without explosions.

(e) The cake must be evenly dried out and baked and should be tested for hardness before being removed from pan.

(f) Each cake should be tested individually after removal and cooling, and if not a good sample, reduced to dust for recaking.

(g) The cake must be absolutely cold before crushing, if the maximum yield of the correct size is to be obtained.

(h) The mass for platinizing should not be ground for 2 or 3 days, as a good sample of cake becomes harder on storage. Bad mass, on the contrary, deteriorates.

Platinizing. The mass is first carefully riddled over $\frac{1}{4}$ " mesh to free from dust, and is then placed in pottery trays, on rubber mats, in lots of 200 lbs. This with a 9%–10% water content, is equivalent to 180 lbs. MgSO_4 . The amount of platinum chloride required to give a 0.3% platinum content, is then weighed out and dissolved in about $2\frac{1}{4}$ gals. of water. This is evenly sprayed over the mass, which is continually raked over to expose a fresh surface. A glass spray is used, and the head to produce spraying is secured by raising the solution container to the necessary height by means of pulleys. Heat is evolved during spraying, and after all the solution has been disposed of, the mass is allowed to remain for at least 8 hrs. before being removed to the converters.

Mannheim Oleum Plant. This plant at Queen's Ferry, consists of 10 independent units, 8 being equipped with 12 lump burners each, the remaining 2 having 2 Herreschoff fines mechanical burners, and 2 lump burners each.

Pyrite Crushers. The pyrites is received in lump form, and is stored in the pyrites shed until required for use. It is then loaded by hand into bogies which are pushed along the track to the crusher, being finally drawn up to the crusher level by a

motor driven rope haulage and tipped on to the feed of the Blake jaw crusher. The joggle plates are pitched so as to give the maximum amount of ore at the size ($2''$ $2\frac{1}{2}''$) required for the lump burners. After crushing the ore is delivered to a rubber belt conveyed to a rotary trommel screen, where it is graded as follows: (a) Fines—for export or use on Herreshoff burners. (b) Middlings—to rolls. (c) Lumps—for lump burners. The lumps and fines are trucked to storage or burners, while the middlings are passed through a roll crusher and crushed to fines, passing again to the belt conveyor for screening. The capacity of the plant has been redesigned, but owing to the shutting down of the plant, the necessary reconstruction has not been put in hand.

Burners. About 5-6 tons of ore per day are fed to each unit. The lump burners are of the ordinary type, with a hearth area of 21.4 sq. ft. or 256.8 sq. ft. in all per unit. They are built in sets of 6, the brick-work being sheathed in steel casings, which also encloses along with the burners the two oxide shafts, the platinum shafts and the forewarmer pipes. The burners are charged every 6 hours, at intervals of 3 hours, and dropped twice a day, in order to secure a uniform percentage of SO_2 in the burner gas. The operation of the burners has been the weakest spot in the working of the Queen's Ferry plant. A 10" bed was the normal practice originally. This depth was increased experimentally to 20", but it is difficult to decide as regards the relative advantages of the two practices as, since only one unit has been running, equally good results have been obtained with both methods.

Air Drying Towers. The air for the combustion of the pyrites is forced, by means of a Sturtevant fan, through 2 lead drying towers in series, which serve two units. The towers are 18' x 6 $\frac{3}{4}$ ' by 5' 4" and 12' x 6 $\frac{3}{4}$ ' x 5' 4" respectively, brick lined and packed with 2" 4" coke supported on a brick-work grid 30" from the base. 94% sulfuric acid is circulated over these towers by means of a Kynock centrifugal pump. 1 pump feeding 3 drying towers, and a second feeding the drying systems of the other two pairs of units. The circulation acid is kept at 94% by a constant inflow of 98% acid, and a constant outflow of 94%, the latter acid being utilized as feed for the unit. The efficiency of the air drying system on this practice is 95%-96%. A slight positive pressure is maintained at the burners by means of a main

dampers on the air fan outlet, and also by regulation of the dampers on the individual burners.

Oxide Shafts. There are two oxide shafts to each battery of six burners, i. e., 4 per unit, each shaft consists of a sq. steel brick lined chamber 22 sq. ft. in internal cross section, and measuring 10 ft. from the base of the crown of the arch through which the gases pass to the forewarmer. The shaft is filled with 2" burnt oxide specially picked and screened for this purpose. Each day 2 cwts. fresh oxide is fed into each shaft through a sealed hopper, and an equivalent amount shaken out of each at the bottom through the movable bars. About 40%-50% conversion takes place in the oxide shafts if they are properly operated. The gases pass from the oxide shafts to the forewarmer chambers (see later), where they are cooled by the gases going to the superheaters for the platinum shaft, and pass then to the oxide shaft coolers through 10" diameter pipes.

Oxide Shafts Coolers. There are 3 oxide shaft coolers per unit of 12 burners. These are mild steel cylinders 3' 7" in diameter x 16' 5" high, flanged at the bottom and fitted to a cast iron base with acid and sludge outlet connections. Each cooler is fitted with 4 baffle plates placed at 3' 2" intervals, the gases passing first through 2 in parallel, both being connected to the third cooler.

Oxide Absorption Towers. The gases pass from the coolers to the 2 oxide absorption towers. Each consists of a mild steel shell, 8' in diameter x 24' high, lined with acid proof tiles. The packing is of quartz carried on an iron grid from the base of the towers. Acid is circulated over the towers by Kynock centrifugal pumps. The gases are drawn through the absorption towers by a 12" Kynock fan belt driven from a 10 h. p. motor at about 1700 r. p. m. The mist deposited at the fan is collected through a seal into the waste acid tank, the contents of which are periodically pumped to the TNT acid system.

Acid Catchers. The gases from the main fan are forced through 4 acid catchers in parallel. These are mild steel tanks 11' 6" x 6' 6" x 4' 1", and are packed with graded quartz on a steel bar grid as follows: 4" of 4" quartz; 6" of 3" to $\frac{3}{8}$ " quartz; 20" of $\frac{1}{4}$ " to $\frac{1}{20}$ " quartz. The gases pass from the bottom to the top, the acid deposited being drained away through lutes and

passing to the waste acid tanks. The volume of the gas is then divided into two, half passing through each set of filters in parallel.

Filters are of the same design as the acid catchers, but are filled with basic slag, the gradings for which are the same as for the quartz on the acid catchers, with the addition of a 3" layer of lime asbestos at the top. The filtering and scrubbing system on a Mannheim unit is very inadequate, the gases often reaching as high a figure as 0.095 grain per cu. meter.

Heat Exchanger or Preheater. The gases from each set of the filters then pass through a 12" main to a heat exchanger, where they are heated up at the expense of the hot gases leaving the platinum shaft. Each heat exchanger consists of a mild steel cylinder 4' in diameter x 16' 10" long, containing a battery of 104—2³/₄" steel tubes built on lines similar to the heat exchanger on the Grillo plant. The gases leave the heat exchangers at about 220°–240°, efficiency being approximately 87%, and the rate of heat transference is 400 C. H. U.'s per sq. ft. per hour.

Forewarmer. The gases then pass to the forewarmer, where a further heat transference takes place at the expense of the hot gases leaving the oxide shaft. The forewarmer consists of a series of 12 horizontal pipes, 10" diam. x 12¹/₂' long, arranged in 2 parallel sets of 6 pipes each, leading into a common header to the superheater. The pipes are arranged over the arch of the two oxide shafts and the gases leave the forewarmer at a temperature of about 370°. The efficiency of the forewarmer is about 87% with a heat transference of 135 C. H. U.'s per sq. ft. per hour.

Superheater. The gases then pass to the coke-fired superheater, where they are heated to the 480° necessary for effective conversion in the platinum shaft. The superheater consists of 3 series of two vertical pipes, each being 11¹/₂' long x 10" diam. Its efficiency is very low—just under 10%.

Platinum Shafts. These are 2 per unit, situated between each pair of oxide shafts, each consisting of 3 ovens 1' deep, by 4¹/₄' x 2' 3", into each of which is placed a set of 10 platinized mats, supported between wire gauzes, the whole being bound in a cast iron frame. Recently the number has been increased to 15 mats per oven. The mats are made of ¹/₄" asbestos woven at ¹/₈" mesh, 24 gm. platinum being deposited upon each mat.

After leaving the platinum shafts, the gases pass through the heat exchangers to the platinum cooler shaft, which is of the same dimensions and designs as the oxide coolers. From here the gases pass to a series of 3 absorption towers similar to those previously described.

Mannheim Platinizing Process. 40 liters of pure distilled water are placed in an enameled bath. To this is added 1 liter of a solution of Na_2CO_3 containing $\frac{3}{8}$ lb., the whole is heated to boiling point by means of steam at about 20 lbs. pressure and as soon as the liquid boils vigorously, the asbestos mat which has been shaken to remove loose particles, is placed in the bath. 1 liter of sodium formate solution containing 1 lb. pure HCOONa is added, and after bringing the liquid again to the boiling point, 400 cc. of 10% PtCl_4 solution previously made alkaline with Na_2CO_3 are poured in slowly, the mat is moved up and down slowly through the solution 3 or 4 times, and then a cover is placed on the bath and the liquid allowed to boil for $\frac{1}{4}$ hour. The mat is reversed and a further 200 cc. of PtCl_4 solution added, after which the solution is kept at the boiling point until the whole of the Pt has been deposited on the mat. This takes from 10-20 minutes, and is shown by the complete clearing of the soln. The mat is then reversed, and placed in another bath containing 50 liters of cold water. When 10 mats have stood in this bath for from 4-5 hours, the water is run off and replaced by 60 liters of a 10% H_2SO_4 wash at a temperature of $35^\circ-40^\circ$. This first acid wash lasts 18 hours and is followed by a second 10% H_2SO_4 wash, lasting the same time and at the same temperature. The acid treatment is followed by two hot water washings, each lasting from 10-12 hours, which remove the soluble phosphates formed during the treatment with H_2SO_4 . The mats are then placed on wooden racks in a hot air oven, at about 60° , to drain and dry. After drying they are ready to be mounted for baking in the platinum shaft. The mats are mounted as follows: (a) Heavy iron frame with handle; (b) iron wire grid; (c) platinized mat; (d) light iron frame; and so on until 10 mats are in position. The complete element is now placed in one of the sections of the platinum shaft, and baked for 5-6 hrs. at a temperature of 450° . After baking, the element is dismantled and the mats placed carefully (as they are very brittle) into a tank filled with cold dis-

tilled water, where they are left for about 2 hours until they are quite pliable, the water is then run off and a 10% solution of HCl added and kept by means of steam at about 50° for 12 hours. After this follow two hot water washings, each lasting 6 hours, and finally 1 cold water wash lasting the same time. The mats are then drained on racks and sprinkled with cold distilled water, until the water draining from the mats shows no trace of either chloride or sulfate. The mats are then drained, dried and are ready for use. It is important to test the distilled water systematically, as the presence of any impurity effects the deposition and adherence of the black platinum on the asbestos.

Retreatment of Mats for Removal of Arsenic. After the removal of an element from the plant, samples are taken from the 3rd and 6th mats, and the As per cent. determined. The mats are then given a 5% HCl wash at 60° for 6 hours, then washed twice in hot water and finally drained and sprayed with distilled water until the water issuing from the mat shows no trace of sulfate or chloride. The mats are then dried and samples again taken to determine the arsenic as in the retreated mat.

The Freiburg Process. The contact process of the Mulderer-Huette of Freiburg, due to C. Winkler,¹ was commenced in 1876, for the manufacture of oleum from sulfur dioxide and oxygen produced by Deville's process of splitting up sulfuric acid at very high temperatures, and drying the gases. In 1878, Winkler found it possible to use gases from pyrites burners, and thus anticipated the Badische patents by about 20 years. The process is carried out as follows:

- (1) The burner gas is produced in ordinary kilns from pyrites containing only a small amount of arsenic.
- (2) The gases are drawn from the kilns by fans through the purifiers, and then forced from these to the contact apparatus.
- (3) The purification of the gases is effected entirely by filtration, without any washing or drying apparatus. Filtration is made through cotton-wool, which may be partly replaced by wood-shavings. The gas passes through the dust-flues, and then through lead towers packed with coke, charcoal, wood-shavings,

1. Dingl. Poly. 1875, **218**, 128; abst. J. C. S. 1876, **29**, 783; Bull. Soc. Chim. 1876, **25**, 43; Chem. Centr. 1875, **46**, 755; Chem. Tech. Rep. 1875, **14**, 1, 221; Jahr. Chem. 1875, **28**, 161; Wag. Jahr. 1875, **21**, 296.

and cotton, preferably but not necessarily in the order given.

(4) Formerly platinized asbestos, containing 40%–50% of platinum, prepared by the formate method (p. 1113) was used in the converters. In 1883 platinized pumice was substituted, but in 1888 this was replaced by platinized unglazed porcelain. The contact mass is contained in horizontal iron retorts. The gas containing 6% SO_2 and is passed through five retorts, heated by a producer to $440^\circ\text{--}460^\circ$, yielding 20 to 24 cwts. SO_3 per 24 hours.

(5) Absorption is effected in vertical towers fed with concentrated sulfuric acid until a strongly fuming acid is formed. If anhydride is required, this is distilled in iron retorts.

The Rabe Process. In the process described in the patents of H. Rabe¹ the gas enters by a lined cast-iron pipe provided with cleaning holes, and sufficient water or sulfuric acid is introduced by a Koerting's spray to be completely vaporized. The partially cooled gas then passes to a Glover tower constructed in the usual way and fed with cold strong sulfuric acid, which completes the cooling and removes dust, which passes out with the hot acid in the form of mud.

The cooled gas is next forced to the filters, consisting of a lead box containing graded coke supported on a grid, the granule size of the coke varying from 10 mm. below to 1 mm. above. A large surface is thus exposed to prevent obstruction of the draft, the filter being periodically washed. Asbestos may be used instead of the finest coke. The gas should now be optically clear.

To remove gaseous impurities, especially HCl , the gas is next passed over sodium bisulfate in a chamber provided with shelves, or in the form of a concentrated solution in a scrubber. The gas now passes through a second Glover tower fed with strong sulfuric acid, and then to the contact apparatus.

In this the catalyst is spread on sieves in comparatively wide chambers, and it is possible to carry out the reaction with different contact masses, or different temperature, or "combinations of

1. E. P. 3327, 1901; abst. J. S. C. I. 1902, **21**, 407; Chem. Ztg. 1902, **26**, 585; Mon. Sci. 1903, **59**, 75. Hung. P. 21959, 1901. D. R. P. 143593; abst. Zts. ang. Chem. 1903, **16**, 1183; Chem. Zts. 1904, **3**, 291, 337; Chem. Ztg. 1903, **27**, 1138; Wag. Jahr. 1903, **49**, I, 258; Mon. Sci. 1904, **61**, 82. See H. Niedenführ, Zts. ang. Chem. 1900, **13**, 960. D. R. P. 111019, 112835.

both." The SO_3 is absorbed in reaction towers fed with sulfuric acid.

No further details of this process appear to have been given; it has been used in several works and is said to be cheap and efficient.

The Properties of Oleum. What is technically called Fuming Sulfuric Acid is pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, or fuming O. V., containing 45% SO_3 . Acids containing less than 30%, or between 60% and 70% are liquid at the ordinary temperature, the remainder being solid, and liquefiable at temperatures not exceeding 36° . The liquid fumes strongly in moist air, and on heating sulfur trioxide passes off. All acids containing free SO_3 are now given the name "Oleum."

The properties of oleum have been given by R. Knietsch,¹ but there is little doubt that many of his figures are inaccurate,² the specific gravities given by this observer (see Chapter VIII) probably being too high. The following figures refer to acids produced in a British works:

| Per cent. SO_3 | Specific Gravity at 15° |
|-------------------------|-----------------------------------|
| 18 | 1.8955 |
| 19 | 1.9008 |
| 20 | 1.9055 |
| 21 | 1.9110 |
| 22 | 1.9160 |

The temperature correction is found, per degree, as follows:

| | |
|-------------------------|-----------------|
| 10° – 20° | subtract 0.0015 |
| 20° – 55° | subtract 0.0010 |
| 55° – 60° | subtract 0.0020 |

Contact Processes in the United States. In 1898 the Badische Co. erected an experimental plant in New Jersey, and the Knietsch patents were subsequently acquired by the General Chemical Co., who have also taken out patents for the contact process.³ The Schroeder-Grillo process has been worked since 1899 by the Mineral Point Zinc Co. at their works in Wisconsin. In 1900

1. R. Knietsch, Ber. 1901, **34**, 4100; abst. J. C. S. 1902, **82**, ii, 132.
2. A. Porter, Trans. Faraday Soc. 1918, **13**, part 3; abst. J. S. C. I. 1918, **37**, 9 R, 27-A; C. A. 1918, **13**, 1970.
3. G. Lunge, Zts. ang. Chem. 1910, **23**, 721; abst. C. A. 1910, **4**, 1897; see also U. Wedge, Eighth Intl. Cong. Appl. Chem. 1912, II, **2**, 241; abst. J. S. C. I. 1912, **31**, 874. T. Briggs and H. Merriam, U. S. P. 1013638, 1912; abst. C. A. 1912, **6**, 671; Chem. Ztg. Rep. 1912, **36**, 194; Mon. Sci. 1912, **77**, 130. U. S. P. 1082301; abst. C. A. 1914, **8**, 792; Mon. Sci. 1914, **81**, 65.

the General Chemical Co. commenced the use of the Herreshoff system, described below; in the New York works, pyrites gases being used. This company has acquired the rights of the Badische, Meisler, Lucius and Brüning, Tentelaw, and Rabe patents. The other companies using contact processes are, for the most part, their licensees. The New Jersey Zinc Co. owns the Schroeder-Grillo patents for the United States. About one-quarter of the acid made in the States is said to be manufactured by the contact process.¹ Contact processes were tried by the Tennessee Copper Works, but have been abandoned for the use of large lead chambers.²

Miscellaneous Contact Processes. I. P. Lihme, assignor to the Grasselli Chemical Co. of Cleveland, Ohio, states³ that the arsenic in burner gases exists in the form of arsenous hydride, AsH_3 , produced by the action of metal, such as iron, on sulfuric acid containing arsenious oxide, As_2O_3 , and devised a special form of apparatus for removing this impurity (Fig. 105). The arsenous hydride is not removed by absorption towers and filters, and arsenic is not completely retained by an oxide of iron shaft, but is eliminated by passing the gases over iron or copper oxide heated to a temperature not exceeding 100° , and preferably 70° to 90° . The apparatus consists of a furnace 1, iron contact tower 2, cooler 3, and primary absorption towers 4, as in the ordinary plants. After leaving the absorption towers the gases pass through a slag-wool filter 5, but are not then passed to the platinum contact mass included in the tower 2 as usual, but first through an iron shaft or tower 6, provided with grate bars 7, to contain the iron or copper oxide, which is used as the arsenic eliminating material. This is provided with hoppers 8 on top for charging fresh materials, and also with steam coils 14, preferably several coils under the bars, for heating the contents of the tower to the requisite temperature. Additional coils are provided on the top of the tower to give the gases the required temperature before entering the iron shaft. Additional filter boxes 9, similar to 3, are installed

1. F. Quinke, Zts. ang. Chem. 1910, **23**, 1923.

2. W. Freeland and C. Renwick, Eng. Min. J. 1910, **89**, 1116; abst. Chem. Ztg. Rep. 1910, **34**, 372. See also G. Patterson and L. Cheney, Eight Intl. Cong. Appl. Chem. 1912, 215; J. Ind. Eng. Chem. 1910, **4**, 723; abst. C. A. 1913, **7**, 869; J. S. C. I. 1912, **31**, 1028.

3. U. S. P. 1103522, 1914; abst. C. A. 1914, **8**, 3102; Zts. ang. Chem. 1916, **29**, 116; Chem. Ztg. Rep. 1915, **39**, 114; Mon. Sci. 1914, **81**, 178.

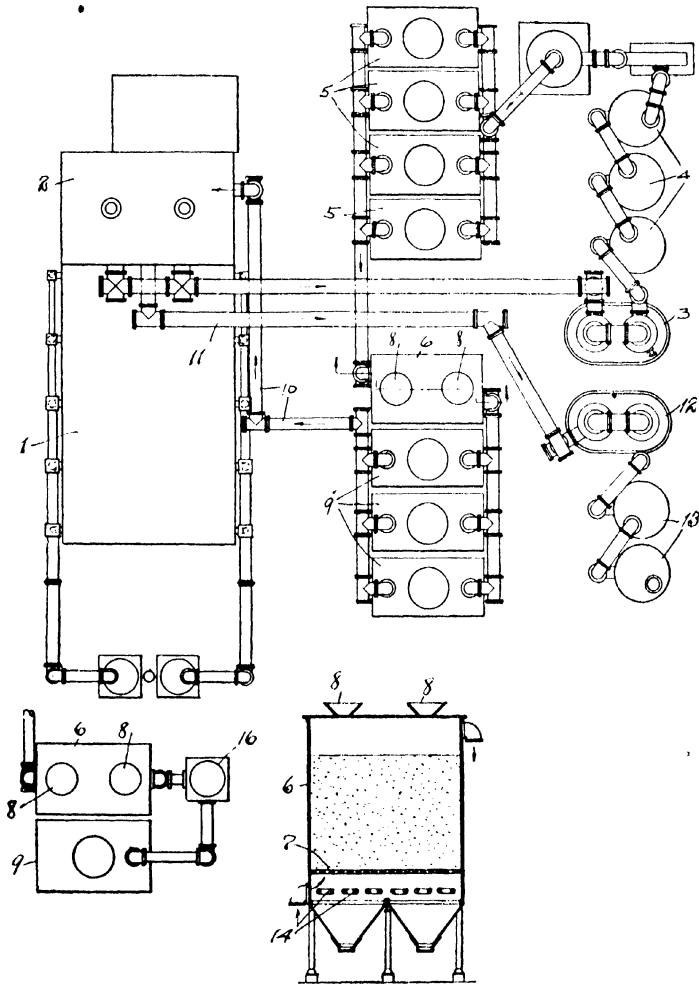


FIG. 105.—THE LIME PROCESS OF SULFURIC ACID MANUFACTURE

in the path of the gases leaving the special iron shaft, and the gases pass to the platinum contact chamber by a pipe 10, being then carried by a pipe 11 to the second cooler 12, and the final absorption tower 13. The special point of the process is the recognition of the presence of arsenous hydride in the gases, and the steps taken for its removal. If, however, the kiln gases are

carefully dried, as directed in the Mannheim patents, it is difficult to see how arsenous hydride can be produced, as claimed, by this inventor. The water produced by the oxidation of arsenous hydride in the tower 6 is absorbed in a lead tower 16, filled with coke over which strong sulfuric acid trickles.

In the patents of R. Raynaud and L. Pierron,¹ reference is made to carrying out the conversion in distinct stages. At first, a portion of the sulfur dioxide and oxygen are combined, then the remainder of the two gases, and lastly such portions of the gases

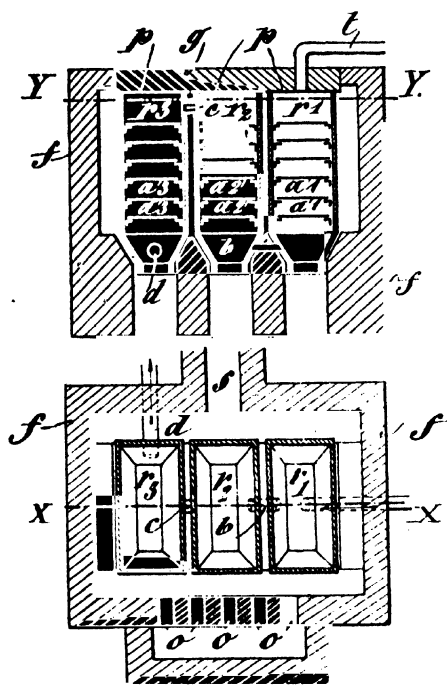


FIG. 106.—RAYNAUD AND PIERRON PROCESS OF MAKING SULFURIC ANHYDRIDE

as are produced by the decomposition of the sulfur trioxide formed.

The temperature is kept uniform, contact masses containing but a small proportion of platinum are placed near the inlet of the gaseous mixture, and then substances containing less plat

1. U. S. P. 751941, 1904; abst. Chem. Zts. 1904, **3**, 492; J. A. C. S. 1904 **26R**, 404; Mon. Sci. 1905, **63**, 7. U. S. P. 736876, 1903; abst. Chem. Zts. 1904, **3**, 82; J. A. C. S. 1904, **26R**, 141; Mon. Sci. 1903, **59**, 182.

inum. In the intermediate stages the gases come in contact with masses richer in platinum. The apparatus (Fig. 106) comprises three vessels r_1 , r_2 , r_3 , provided with covers, p , p , enclosed within brick walls, f , f . A layer of insulating material g is placed over the covers of the vessels to prevent undue cooling. Around the vessels hot gases from a producer or furnace circulate, entering through the passages o , o , provided with dampers, and escaping through a passage s . Inside the vessels are superposed shelves or sieves, a_1 , a_2 , a_3 , respectively, upon which are placed the catalytic substance. The mixture of sulfur dioxide and air, which may have been previously purified, enters the first vessel r_1 , through the pipe t in the cover, and passes down through the catalytic material on the sieves a_1 , then through a pipe b to the lower part of the second vessel r_2 , up through the catalytic substance on the sieves a_2 , then through a pipe c to the upper part of the third vessel r_3 , and down through the catalytic substance on the sieves a_3 . The gas then escapes through the pipes to the absorption apparatus. In the first vessel r_1 are placed catalytic substances containing, say, up to 5% of platinum, in the second vessel r_2 substances containing say, 40% of platinum, and in the third vessel, r_3 , substances containing, say, 10% of platinum near the gas inlet, the percentage of platinum decreasing as the substances are placed nearer the outlet. The actions previously described then occur.

In the second patent of these inventors, a catalytic mass of constant composition is used, but the temperatures are varied. In the first vessel it is 300° , in the second vessel 500° , and in the third vessel 400° ; at the latter temperature recombination of the dissociated sulfur trioxide takes place.

The apparatus is shown in Fig. 107 and consists of a set of ovens F_1 , F_2 , F_3 , each containing a cylindrical vessel in which are superposed sieves upon which is placed the contact mass of uniform richness in platinum, say 10%. The ovens are at a distance from one another, and each is heated separately by furnaces G_1 , G_2 , G_3 , or by hot gases. The sulfur dioxide gases enter by a pipe T into the upper part of the first vessel C_1 , from the lower part of which they pass through a pipe T' into the upper part of the second vessel C_2 . They leave this second vessel at the lower part and pass into the upper part of the third vessel through

a pipe T_2 , in which they may be cooled by air or water circulating through a coil S . From the lower part of C_3 the gases pass to the absorption apparatus. To avoid a rise of temperature in the third vessel C_3 , sufficient to cause dissociation of sulfur trioxide, two similar vessels C_3 , located in separate ovens as shown, may be used, and the gases caused by the dampers t_1 , t_2 , to pass

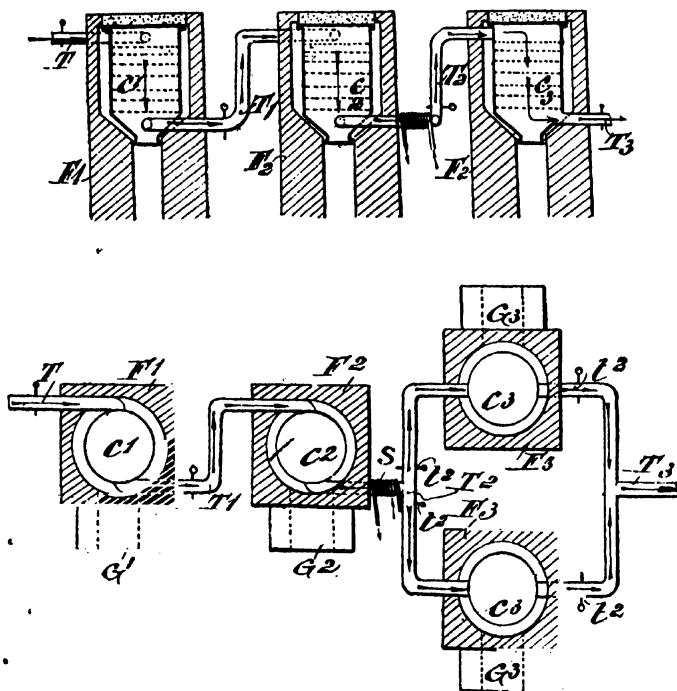


FIG. 107.—RAYNAUD AND PIERRON SULFURIC ANHYDRIDE PROCESS

through the second vessel when the first has become heated throughout.

H. Blackmore¹ describes a process for preventing undue rise of temperature during the union of the gases by mixing with them

1. U. S. P. 769585, 1904; 778099, 1904; abst. Chem. Zts. 1904, **3**, 763; 1905, **4**, 270; J. A. C. S. 1905, **27R**, 296, 502; Mon. Sci. 1905, **63**, 54, 116. U. S. P. 828268, 1906; abst. Chem. Zts. 1906, **5**, 496; Mon. Sci. 1907, **67**, 53. See also U. S. P. Re-11995, 1902.

gases which undergo chemical changes with absorption of heat. This process is described as "chemical refrigeration." Carbon dioxide and nitrogen dioxide are directed to be used, these being reduced by absorption of heat to carbon monoxide and nitric oxide, which are afterwards re-oxidized in a separate portion of the apparatus.

G. Stone¹ has disclosed a new form of contact vessel, shown in Fig. 108, which consists of a series of individual superposed sec-

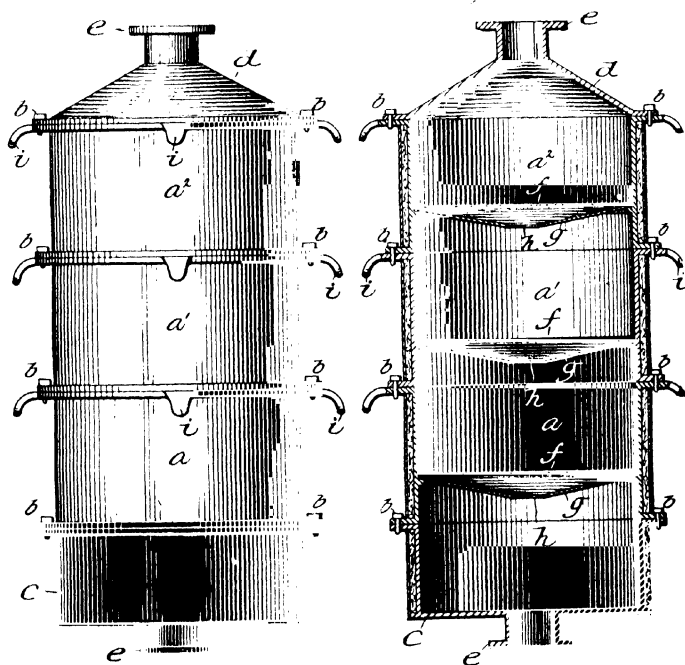


FIG. 108. — THE STONE APPARATUS FOR H_2SO_4 MANUFACTURE

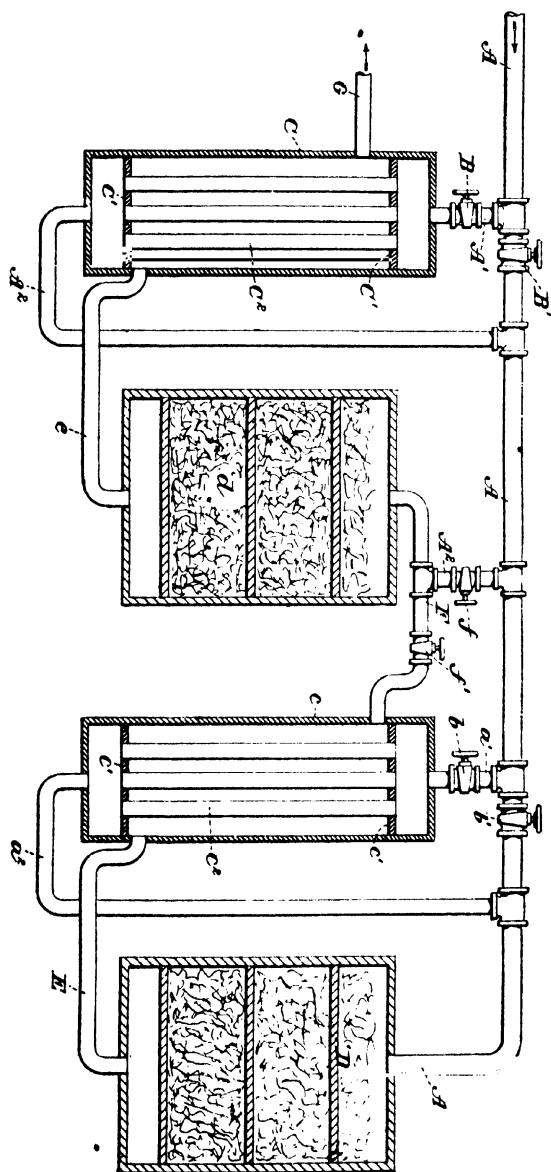
tions a , a_1 , a_2 , which may conveniently be cylindrical, and jacketed with non-conducting material. The sections are flanged at the top and bottom, and provided with dowel-pins b , fitting in corresponding recesses. The series of sections rests upon a fixed section c , and is surmounted by a roof-section d . Each of the

1. U. S. P. 711186, 1902; abst. Chem. Zts. 1903, **2**, 158, 274; J. A. C. S. 1903, **25R**, 242.

sections *a* is provided with a screen *f* to support the contact mass, and it is also desirable but not essential that a diaphragm *g*, having a central orifice *h*, be inserted between each screen to aid mixing. The preheated gases are passed into the apparatus, preferably from below upwards. The contact mass may be renewed in the sections separately, as required. New sections may be inserted to take the place of those taken out for renewal. These new sections being put on top of the apparatus, so that the nearly converted gases pass through the most active section.

A series of patents have been taken out by the General Chemical Co. of New York. In the first of these¹ a contact apparatus is described having a plurality of contact chambers and a plurality of heat-exchangers (Fig. 109) in which *A* is the inlet main, connected through *A'* by a valve *B* to the heat-exchanger *C*, from which a pipe *A*₂ leads back to the supply pipe, a valve *B'* being interposed between the two sections. At a further point is located a heat-exchanger *c*, with connections *a*₁ and *a*₂. The end of the pipe *A* is connected with the contact chamber *D*, of suitable construction, but may be much shorter than those previously employed. It may also contain contact material increasingly richer from the inlet towards the outlet. The pipe *E* connects the contact chamber outlet with the inlet of the exchanger *c*. From this a pipe *F* leads to another contact chamber *d*, the outlet pipe *e* of which is connected with the central chamber of the exchanger *C*. From this passes the outlet pipe *G* to the absorption apparatus or a second or third, etc., contact plant. In the normal operation of the apparatus the valves *B'* *b'* may be closed at first while the valves *B* *b* are open. This will cause the incoming gas mixture first to enter the exchanger *C* and pass through the central portion of the supply-pipe *A*, then to pass through the exchanger *c*, and finally to the first contact chamber *D*. The partially converted mixture flows through the pipe *E*, the central chamber of the exchanger *c*, and the pipe *F* to the second contact chamber *d*, where the reaction is continued, possibly to completion. The gas then passes through the pipe *e* and the central chamber of the exchanger *C* to the outlet *G*. The incoming gas thus comes into heat exchange with the partially con-

1. J. Herreshoff, U. S. P. 719333, 1903; abst. Chem. Zts. 1903, **2**, 529; J. A. C. S. 1903, **25R**, 378; Mon. Sci. 1903, **59**, 100.

FIG. 109.—THE HERRESHOFF APPARATUS FOR SO_2 MANUFACTURE

verted product twice in succession, being first heated with the product nearest completion. Thus by the time the incoming gas reaches the contact chamber *D* it is heated to the temperature of reaction. If the combined effect of the two exchangers *C* and *c* is too energetic, a portion only of the entering gas is passed through them, or only one is used.

In the second patent¹ the gaseous mixture is gradually diluted during the conversion. The inlet is at *A* (Fig. 110), and *B* is the first contact chamber, from which a pipe *C* leads to the second chamber *B*₁, the outlet of which is another connecting pipe *C*₁ leading to the third contact chamber *B*₂. The outlet is at *D*. At least two chambers are used. Each connecting pipe is provided with a branch *E*, controlled by a valve *F*, and in connection with a fan *G*. The burner gas is admitted at *A*, but contains a larger proportion of sulfur dioxide, say 11%, than usual. The mixture after passing through *B* becomes poorer in oxygen and heated. It is cooled and admixed with cool air or oxygen before passing to the next contact chamber, the air being admitted through *EE'* from the fans *G'*. The operation is repeated after successive contact chambers. The use of a stronger initial mixture reduces the cost and size of the purifiers, and on account of the lower amount of free oxygen there is less likelihood of sulfur trioxide being formed before the gases reach the contact apparatus.

The third patent² relates to the absorption of sulfur trioxide. The apparatus (Fig. 111) consists of an absorption tower *A* filled with coke, etc., with an inlet *C*. In the upper part of the tower is a spraying device *D*, through which liquid acid is distributed. The exit is at *E*. The acid for absorption is contained in *G*, connected with *D* by a pipe *H*, with a controlling valve *I*, *J*. The acid after having absorbed sulfur trioxide is discharged through a pipe *K*, to a tank *L*. This tank is divided into two compartments by a partition *F*, acting as an overflow into the second compartment, which is connected by a distributor *M* with a cooling tank *N*. To the acid in *N* is added an amount of water or weak

1. W. Ferguson, U. S. P. 723596, 1903; abstr. Chem. Zts. 1903, **2**, 505; J. A. C. S. 1903, **25R**, 494; Chem. Ztg. 1903, **27**, 372; Mon. Sci. 1903, **59**, 170.

2. J. Herreshoff, U. S. P. 737625, 1903; abstr. Chem. Zts. 1904, **3**, 117, 291; J. A. C. S. 1904, **26R**, 190; Mon. Sci. 1903, **59**, 183.

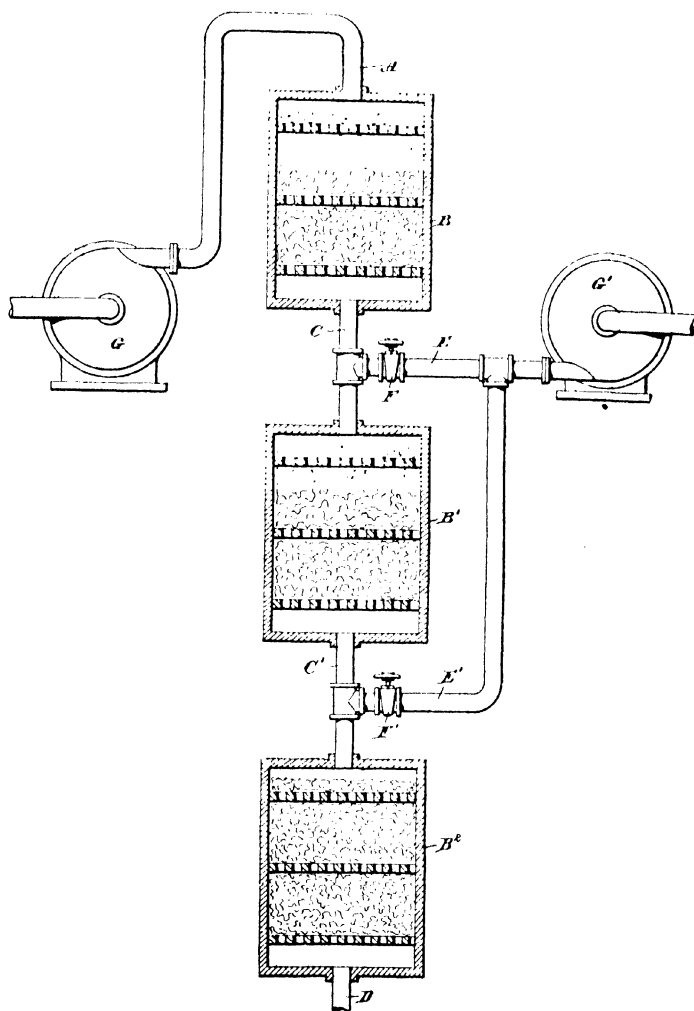


FIG. 110 --FERGUSON PROCESS OF MAKING SULFURIC ANHYDRIDE

acid to bring it to the strength of the original acid in *G*. This water or weak acid is added through the pipe *O*. An overflow pipe *P* takes the cool acid to the tank *Q*, which is called the regulator-tank, and contains a float *R*, connected with the valve *S*, controlling an outlet pipe *T* leading from the tank *L*. The

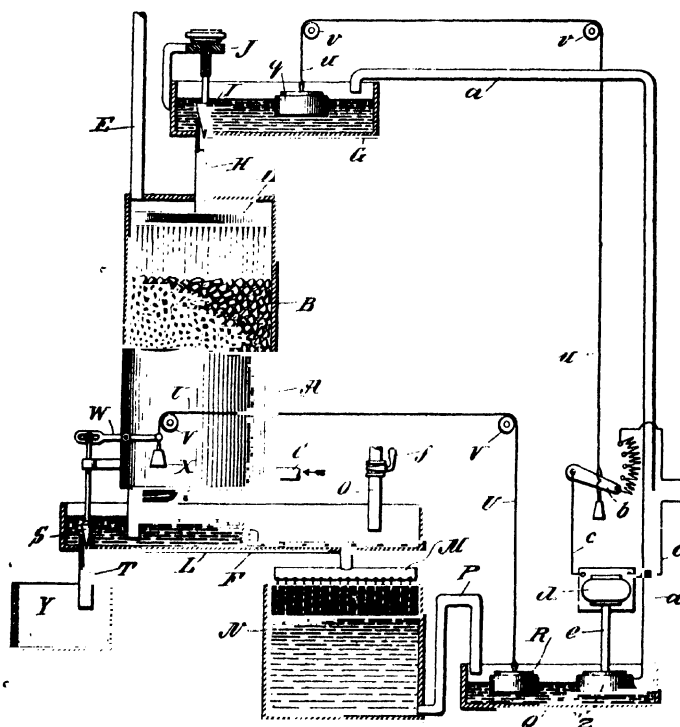


FIG. 111.—HERRESHOFF PROCESS FOR MAKING SULFURIC ACID

connection may consist of a wire *U*, passing over rollers *V*, and connected with a lever *W* which engages the valve stem. A weight *X* keeps the wire *U* taut and tends to open the valve *S* when the float rises. When the float sinks, it will pull up the weight *X* and close the valve *S*. This device ensures the proper proportioning of the strong acid and water or weak acid. A pump *Z* in the tank *Q* discharges through *a* to the supply tank *G* in which

is another float q , from which the wire u leads over rollers v to a device controlling the speed of the pump, which is shown as a rheostat. Acid of 97% may be used to supply the tank G .

The absorption apparatus of I. Cox has already been referred to.¹ Sulfur trioxide at an initial temperature between 95° F. and 115° F. is passed through an absorbing tower down which the absorbing acid, which must be initially between the same limits of temperature and at least 43 times by weight the amount of sulfur trioxide is caused to flow. The acid is circulated, and cooled between each passage through the tower.²

Lead Chamber Process of Sulfuric Acid Manufacture. A

1. I. Cox, U. S. P. 1002824, 1911; abst. J. S. C. I. 1911, **30**, 1210; C. A. 1911, **5**, 3911; Chem. Ztg. Rep. 1911, **35**, 515. E. P. 8528, 1911; abst. C. A. 1912, **6**, 2825; J. S. C. I. 1912, **31**, 187. Can. P. 127540, 1911; abst. C. A. 1912, **6**, 797.
2. For other processes of producing SO_3 , see E. Reynaud and L. Pieron, E. P. 16253, 1900; abst. J. S. C. I. 1901, **20**, 42; Chem. Ztg. 1902, **26**, 53. T. Meyer, Zts. ang. Chem. 1906, **19**, 1313. R. Messel, E. P. 22672, 1909; abst. J. S. C. I. 1910, **29**, 1250; Chem. Ztg. Rep. 1911, **35**, 3; Mon. Sci. 1914, **81**, 82. F. P. 414387, 1910; abst. J. S. C. I. 1910, **29**, 1203. D. R. P. 226331; abst. C. A. 1911, **5**, 1326; Zts. ang. Chem. 1910, **23**, 2098; Chem. Zentr. 1910, **81**, II, 1254; Jahr. Chem. 1910, **63**, I, 508; Chem. Ztg. Rep. 1910, **34**, 510; Wag. Jahr. 1910, **56**, I, 418; Mon. Sci. 1914, **81**, 87. U. S. P. 1078937; abst. C. A. 1914, **8**, 405; Mon. Sci. 1914, **81**, 26. C. Daub, Belg. P. 163431, 1902. H. Hegeler and L. Heinz, U. S. P. 931868; abst. Chem. Ztg. Rep. 1909, **33**, 531. A. Rahtjen, D. R. P. 226107; abst. C. A. 1911, **5**, 1175; Zts. ang. Chem. 1910, **23**, 2293; Chem. Zentr. 1910, **81**, 1103; Jahr. Chem. 1910, **63**, 507; Chem. Zts. Rep. 1910, **34**, 499; Wag. Jahr. 1910, **56**, I, 433; Zts. Schiess. Spreng. 1910, **5**, 440. E. Möller, D. R. P. 270757; abst. C. A. 1914, **8**, 2232; Zts. ang. Chem. 1914, **27**, 220; Chem. Ztg. Rep. 1914, **38**, 159; Wag. Jahr. 1914, **60**, I, 422. F. Curtius, D. R. P. Anm. C-23027. Metallbank u. Metallurgische Ges., F. P. 456524; abst. C. A. 1914, **8**, 1860; Chem. Ztg. Rep. 1914, **38**, 51. P. Babatz, E. P. 1216, 1900. Belg. P. 149757, 1900; abst. J. S. C. I. 1900, **19**, 1110. P. Babatz-Rheingöntheim, D. R. P. Anm. R-43062. Nordyke & Marmion Co., E. P. 1204, 1906; abst. J. S. C. I. 1906, **25**, 536. E. Andersen, D. R. P. 277222; abst. Zts. ang. Chem. 1914, **27**, 577; Chem. Zentr. 1914, **85**, II, 595; Chem. Ztg. Rep. 1914, **38**, 464; Wag. Jahr. Chem. 1914, **60**, I, 576. H. Lelarge, E. P. 18579, 1913; abst. J. S. C. I. 1914, **33**, 906. Farbenfabr. vorm. F. Bayer & Co., D. R. P. 263287; abst. Zts. ang. Chem. 1913, **26**, 562; C. A. 1913, **7**, 4051; Chem. Zentr. 1913, **84**, II, 827; Chem. Ztg. Rep. 1913, **37**, 515; Wag. Jahr. 1913, **59**, I, 515. E. P. 1994, 1912. F. P. 453470; abst. C. A. 1914, **8**, 218; Chem. Ztg. Rep. 1913, **37**, 550. A. Wilhelm, D. R. P. 270062; abst. C. A. 1914, **8**, 1892; Zts. ang. Chem. 1914, **27**, 189; Chem. Zentr. 1914, **85**, I, 712; Chem. Ztg. Rep. 1914, **38**, 101. T. Wolf, U. S. P. 1099530; abst. C. A. 1914, **8**, 2783. B. Parodi-Delfino, E. P. 126390, 1917; abst. C. A. 1919, **13**, 2258; J. S. C. I. 1919, **38**, 395-A, 498-A. H. Meyers, U. S. P. 1314280, 1919; abst. C. A. 1919, **13**, 2742; J. S. C. I. 1919, **38**, 717-A. Soc. anon "La Metallurgie Nouvelle," Belg. P. 164620, 164621, 1902. F. P. 326850, 326851; abst. Chem. Zts. 1903, **2**, 476; Mon. Sci. 1904, **63**, 46. Siemens & Halske Akt. Ges., E. P. 16337, 1901; abst. J. S. C. I. 1902, **21**, 914. British Dyes, Ltd., J. Turner and W. Davidson, E. P. 132923; abst.

general account of the Chamber Process has already been given (p. 1008). The following summary indicates the outlines of American practice.¹ Most of the acid is made from pyrites, the lump ore being imported chiefly from Spain, while the fines are mined in Virginia, Georgia, Tennessee and California. If lump ore is used it is burnt in brick furnaces having grates composed of single square bars which may be turned on their longitudinal axes to let down the burnt ore to the ash-pits. These furnaces hold 3-5 tons each, and are arranged in batteries of 20 to 25 for each set of chambers, the daily charge per furnace being 750-1000 lbs. of pyrites. The burners for fines are cylindrical, containing shelves fitted with scrapers for drawing the ore from shelf to shelf until the fully burnt cinder is discharged at the bottom. The rakes are attached to a central air or water cooled shaft. In one type of furnace the shaft revolves; in another the shaft is rigid while the furnace itself revolves.

The gases from the burners are forced into a dust chamber fitted with baffle plates where oxides of iron, arsenic, lead, zinc, etc., are largely removed. The gases now enter the Glover tower, which consists of a lead tower, usually 20-30 ft. high and 6-8 ft. across, lined with acid-resisting brick and partly filled with quartz or other similar packing, so arranged that the dilute nitrous vitriol distributed by an apparatus at the top may trickle down the interstices. The temperature of the entering gases is 300°-400°, sufficient to drive off the nitrogen oxides from the nitrous vitriol and restore them to the system. The uses of the Glover tower are threefold: (1) to cool the burner gases before entry to the chambers; (2) to restore water and nitrogen oxides to the chambers; (3) to partially concentrate the chamber acid.

From the Glover tower the gases pass to the first of the lead chambers where most of the acid is made. These usually consist of large square or oblong boxes of sheet lead (6 to 8 lbs. to the sq. ft.) and having a capacity of 25,000-75,000 cu. ft. Water in the form of fine spray or steam is blown into the chambers at

J. S. C. I. 1919, **38**, 861-A. United Alkali Co., D. R. P. 157589; abst. Wag. Jahr. 1904, **50**, I, 290. A. Sebillot and L. Maucclair, F. P. 386672; abst. J. S. C. I. 1908, **27**, 690. A process combining catalytic oxidation of SO₂ with electrical precipitation of acid mists formed has been described by H. Welch, Can. P. 194776, 1919; abst. C. A. 1920, **14**, 601.

1. W. Waggaman, Bull. 283, U. S. Dept. Agric. 1915; abst. J. S. C. I. 1916, **35**, 42.

various points. This decomposes the nitrosulfonic acid formed from the sulfur dioxide, oxygen, water and nitrogen oxides into sulfuric acid and returns the nitrogen oxides to the system for further action. The number and size of the chambers used vary from 2 to 10 or more, depending on the capacity of the burners. In large plants the apparatus is often divided into units, each battery of burners having a separate set of chambers. The gases pass in succession through the chambers, and formation of sulfuric acid goes on until up to 98% of the SO_2 is converted into H_2SO_4 .

The residual gases, containing nitrogen, oxides of nitrogen, and a small amount of sulfur dioxide, then enter the lower part of the Gay-Lussac or recovery tower, which is similar in construction to the Glover tower except that it is usually taller and wider (40-50 ft. high and 8-15 ft. diam.) and filled with coke instead of quartz. Strong sulfuric acid (sp. gr. 1.5-1.7) trickles down this tower, absorbing the nitrogen oxides from the residual gases ascending the coke column, which are finally discharged through a stack. The nitrous vitriol formed is pumped to the Glover tower, diluted with water or chamber acid, and distributed as described.

The use of stone,¹ glass,² or a composition of powdered stone and melted sulfur,³ instead of lead for chambers has been proposed, but has not come into use.

As regards the costs of the chamber process, it is stated⁴ that the largest item of expense is pyrites, but the yield per lb. of sulfur burnt is entirely a matter of plant management. The cost due to niter is partly influenced by the design of the towers and the niter-adding arrangements, and the consumption of niter depends primarily on control and chamber space. Labor and power costs, for air compression and pumping water depend on management and maintenance of machinery. The only items appreciably affected by design are overhead costs.⁵

General Construction of the Lead Chamber. It is calculated

1. W. Gossage, E. P. 2982, 1856; 41, 1857.
2. S. Pudney, E. P. 2462, 1862.
3. J. Simon, E. P. 1586, 1859.
4. S. Martenet, Chem. Eng. Manufr. 1916, **24**, 33; abst. C. A. 1916, **10**, 2389.
5. A. Fairlie, Chem. Met. Eng. 1918, **19**, 404; abst. J. S. C. I. 1918, **37**, 652-A; C. A. 1918, **12**, 2412. C. Barber, J. Gas Lighting, 1916, **134**,

that for each kilo of sulfur burnt in the form of brimstone, 6199 liters, and in the state of pyrites 8415 liters, of gas at normal temperature and pressure enter the chambers. Since also the reactions in the chambers occupy an appreciable time, it is evident that sufficient space must be provided. By reason of the corrosive action of the acids, practically only one material can be used for the construction of this reaction space, viz., lead. This is easily rolled into large sheets, from which the walls, roof and bottom of the chamber are constructed.

Lead chambers are always raised above the floor level, so that leakage may easily be detected, and to allow of the accommodation of the other parts of the plant to some extent beneath the chambers. Lunge recommends a height of 17-20 ft. above ground. The foundations should be good; a rocky or pebbly ground is best, marl or limestone, which are dissolved by acid accidentally spilled, are unsatisfactory. The soil may be protected by a layer of asphalt. The chambers are supported on pillars of wood, brick, stone or cast-iron. Up to 26 ft. metal pillars are most useful, although wood or brick are cheapest. Pitchpine is the best wood for all constructional purposes in the

227; abst. C. A. 1916, **10**, 1913. J. Brown and Simon-Carves Bye-Product Oven Co., E. P. 25600, 1912. J. Harris and D. Thomas, E. P. 104461; abst. J. S. C. I. 1917, **36**, 502; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 178. O. Kausch, Chem. App. 1915, **2**, 53, 68; abst. C. A. 1915, **9**, 1372. C. Meigs, U. S. P. 1022493; abst. C. A. 1912, **6**, 1661. "P," Gas World (Coking and By-Products Section), 1918, **68**, No. 1759, 17; abst. C. A. 1918, **12**, 1911. F. Falding, Eng. Min. J. **68**, 441; abst. C. A. 1910, **4**, 1225. T. Harris, Met. Chem. Eng. 1916, **15**, 313; abst. C. A. 1916, **10**, 2966. O. Proelss, Chem. Ztg. 1910, **34**, 1322; abst. C. A. 1911, **5**, 1168. C. de Kalb, Mining Sci. Press, 1918, **116**, 437; abst. C. A. 1918, **12**, 1104. See also Chem. News, 1883, **47**, 266; 1884, **49**, 13. J. S. C. I. 1917, **36**, 491. P. Spence, E. P. 2282, 1857; 863, 1863. H. Baker, E. P. 2065, 1870. A. Upward, J. Bannchr and T. Dale, E. P. 3756, 1869. L. Israel, E. P. 3404, 1868. A. Stinville, E. P. 519, 1903; F. P. 323252, 1902; abst. J. S. C. I. 1903, **22**, 495, 1347. Belg. P. 167784, 1903. The following French patents on lead chamber processes are also of interest in this connection: 323252, 1902; 343156, 347415, 1904; 354831, 1905; 395694, 404071, 1909; 419602, 1910; 431427, 432874, 1911. C. Hinrichs, U. S. P. 9249, 1852. For the manufacture of sulfuric acid by the chamber process and apparatus, see E. P. 1006, 1861; 1352, 2462, 1862; 2593, 1866; 270, 2600, 3036, 1868; 42, 881, 2077, 3494, 1869; 2293, 1870; 176, 1077, 1871; 3189, 1873; 3417, 4342, 1874; 2690, 2873, 1875; 1618, 1877; 1084, 3182, 1878; 3774, 1879; 4522, 1890; 1957, 4888, 1881; 1752, 1882; 3086, 9317, 1884; 15001, 1885; 10798, 12070, 14441, 1886; 9543, 1887; 5058, 1890; 14944, 1891; 16757, 1892; 4342, 1893; 15895, 17602, 1893; 1168, 4856, 13171, 1895; 5012, 1896; 18376, 1898; 10757, 1899; 4272, 1900; 7710, 20142, 20143, 1901; 6051, 26916, 1902; 519, 24619, 1903; 1066, 2541, 6846, 17794, 20012, 1904; 22080, 1905; 18927, 1906; 4861, 11559, 27738, 1907; 11732, 1908; 52, 11128, 26452, 1909.

acid works. In larger works cast-iron pillars are recommended, as they are durable, and may be made higher than wood pillars. Proper brick or stone foundations must be provided for all types of pillars. Joists are placed over the pillars to form the floor on which the chamber rests; the lead should be exposed to air as much as possible.

Many special schemes of construction have been put forward.¹

The Erection of Lead Chamber. The sheet lead used for chambers should be resistant to sulfuric acid, the thickness being usually stated in terms of the weight in lbs. per sq. ft. This should be 6 lbs., sometimes 7 lbs. is used for the ends and top or for the first chamber. The quality of the lead is very important; it appears that pure varieties are more suitable for the purpose.²

1. Awe, Zts. ang. Chem. 1912, **25**, 2523; abst. C. A. 1913, **7**, 869, recommends horizontal suspension. G. Brewer, E. P. 17669, 1902; abst. J. S. C. I. 1903, **22**, 16. J. Harris and D. Thomas, E. P. 6026, 1915; U. S. P. 1203615; F. P. 481471, 1916; abst. C. A. 1917, **11**, 88, 3101; J. S. C. I. 1915, **34**, 1249. E. Hartmann, Ges., E. P. 17035, 1913; abst. C. A. 1915, **9**, 350. Belg. P. 258631, 1913. H. Ising, D. R. P. 267513; abst. C. A. 1914, **8**, 997; Zts. ang. Chem. 1913, **26**, 50; Chem. Zentr. 1914, **85**, I, 87; Chem. Ztg. Rep. 1913, **37**, 694; Wag. Jahr. 1913, **59**, I, 378. W. Jury, U. S. P. 1279119; abst. C. A. 1918, **12**, 2678. T. Kalinowsky, D. R. P. 265640; abst. C. A. 1914, **8**, 409; Zts. ang. Chem. 1913, **26**, 691; Chem. Zentr. 1913, **84**, II, 1630; Zts. Schiess. Spreng. 1913, **8**, 476; Chem. Ztg. Rep. 1913, **37**, 590; Wag. Jahr. 1913, **59**, I, 377. D. R. P. 260991; abst. C. A. 1913, **7**, 3207; Zts. ang. Chem. 1913, **26**, 413; Chem. Zentr. 1913, **84**, I, 188; Zts. Schiess. Spreng. 1913, **8**, 356; Chem. Ztg. Rep. 1913, **37**, 358; Wag. Jahr. 1913, **59**, I, 378. N. Krantz, D. R. P. 283065; abst. C. A. 1915, **9**, 2439; Zts. ang. Chem. 1915, **28**, 248; Chem. Zentr. 1915, **86**, I, 813; Chem. Ztg. Rep. 1915, **39**, 124. Z. Littmann, D. R. P. 271077; abst. Zts. ang. Chem. 1914, **27**, 224; Chem. Zentr. 1914, **85**, I, 1129; Chem. Ztg. Rep. 1914, **38**, 147; Wag. Jahr. 1914, **60**, I, 293. F. P. 462668; abst. J. S. C. I. 1914, **33**, 311. Aust. P. 60969. C. Meigs, U. S. P. 1022493; abst. C. A. 1912, **6**, 1661; Chem. Ztg. Rep. 1912, **36**, 390. A. Nemes, E. P. 24223, 1913; abst. J. S. C. I. 1914, **33**, 593; C. A. 1915, **9**, 1100. F. Neumann, D. R. P. Ann. N 14024, 14025. H. Petersen and H. Ising, D. R. P. 218726, 1908; abst. C. A. 1910, **4**, 2032; Zts. ang. Chem. 1910, **23**, 1052; Chem. Zentr. 1910, **81**, I, 876; Zts. Schiess. Spreng. 1910, **5**, 256; Chem. Ztg. Rep. 1910, **34**, 142; Wag. Jahr. 1910, **56**, I, 411. D. R. P. 295044, 1914; abst. J. S. C. I. 1917, **36**, 503; Zts. ang. Chem. 1916, **29**, 537; Chem. Ztg. Rep. 1917, **41**, 2. Prost, Assoc. Belge des Chim., Dec. 12, 1901; abst. Chem. Ztg. 1902, **26**, 12; J. S. C. I. 1902, **21**, 250. T. Richters, E. P. 4888, 1881. M. Seeck, E. P. 16187, 1904; abst. J. S. C. I. 1915, **34**, 871. F. P. 474302, 1914; abst. J. S. C. I. 1915, **34**, 715. K. Walter and E. Boenig, E. P. 14944, 1891; abst. J. S. C. I. 1891, **10**, 1007. A. Waller and H. Wiegand, D. R. P. 266549; abst. Zts. ang. Chem. 1913, **26**, 685; Chem. Ztg. Rep. 1914, **38**, 62. O. Wentzki, D. R. P. 230534; abst. C. A. 1911, **5**, 2707; Zts. ang. Chem. 1911, **24**, 427; Chem. Zentr. 1911, **82**, I, 521; Chem. Ztg. Rep. 1911, **35**, 95; Wag. Jahr. 1911, **57**, I, 416; Mon. Sci. 1914, **81**, 84; Zts. Schiess. Spreng. 1911, **6**, 96.
2. C. Barrs, J. S. C. I. 1919, **38**, 407-T; abst. C. A. 1920, **14**, 503. See also G. Davis, Chem. Eng. **1**, 142. G. Lunge, Zts. ang. Chem. 1892, **5**,

Analyses of good chemical lead, in per cents., are given below:

| | I | II |
|----------|--------|--------|
| Bismuth | 0.0023 | 0.0139 |
| Iron | 0.0021 | 0.0021 |
| Antimony | 0.0016 | 0.0011 |
| Copper | 0.0008 | 0.0006 |
| Cadmium | Trace | Trace |
| Silver | Trace | Trace |
| Zinc | 0.0009 | 0.005 |

The sheets of lead are first wrapped round a wooden roller, 6 in. thick, and beaten with a plumber's mallet to remove inequalities and indentations.

The "Flash Test" for chemical lead gives a useful indication of its quality, and is performed as follows: A strip of the lead to be tested is hung over the side of a glass beaker to reach within half an inch of the bottom. The beaker is filled one-third full with 96% sulfuric acid so as to cover an inch of the lead strip. A thermometer reading to 400° is suspended in the acid, and a glass tube fitted to a water blower is placed in the beaker so that a steady stream of air can be passed through the acid. The beaker is now heated by a Bunsen and the action on the lead noted as the temperature rises. At a certain temperature the action of the acid becomes suddenly more violent, and solution rapidly takes place. This is known as the "flash-point;" a cloud of sulfate is then formed and the lead completely vanishes in a few seconds. Ordinary plumber's lead flashes at about 160°-240°; good brands of virgin pig lead flash at 240°-265°, while a good chemical lead suitable for acid resisting apparatus should stand up to 280°.

The lead sheets are joined by autogenous welding with a hydrogen flame, an operation known as "lead burning." The apparatus used consists of a hydrogen generator, and a blowpipe and bellows. Straps are welded on the sheets at suitable places for attachment to the supports. The chamber bottom is not 643. J. Mactear, J. S. C. I. 1884, **3**, 230. Eng. Min. J., March 8, 1902; abst. J. S. C. I. 1902, **21**, 510. O. Mühlhäuser, Zts. ang. Chem. 1902, **15**, 758. H. Leyendecker, E. P. 2756, 1901; abst. J. S. C. I. 1902, **21**, 124; Chem. Ztg. 1902, **26**, 560. Chem. Trade J. 1906, **38**, 91. For the action of fluorine on the lead of sulfuric acid chambers, see P. Truchot, Seventh Intl. Cong. Appl. Chem., 1909; abst. J. S. C. I. 1909, **30**, 207; C. A. 1911, **5**, 1918. H. Klenke, D. R. P. 219400, 1908; abst. C. A. 1910, **4**, 2032; Zts. ang. Chem. 1910, **23**, 1052; Chem. Zentr. 1910, **81**, I, 970; Jahr. Chem. 1910, **63**, I, 525; Zts. Schiess. Spreng. 1910, **5**, 174; Chem. Ztg. Rep. 1910, **34**, 159; Wag. Jahr. 1910, **56**, I, 412; Mon. Sci. 1913, **79**, 159.

joined to the sides, but forms a large flat saucer, into which the top part of the chamber dips, the joint being completed by a hydraulic seal of acid.¹

The housing of the chamber depends on the nature of the climate. In England the roofs are always left open to the weather, the sides being protected by light wooden walls. In other cases, as in the north of France, Belgium and Germany, the chambers are enclosed in buildings. Special arrangements for keeping the chambers cool are in use.²

The life of a chamber depends largely on the mode of working. The first chamber is exposed to the maximum wear and tear, those parts which become hotter, wear out first. The chambers should be well supported with straps and maintained in good repair. They may be repaired when necessary by cutting out the worn part and burning on a patch. The roof usually wears out first, then the part dipping into the acid at the bottom, while the lead saucer into which the chambers dip is the last to be replaced. From eight to ten years may be stated as the normal life of the chambers; if carefully worked they may last twenty or even thirty years.³

The size of the chambers has already been considered (p.

1. G. Davis, E. P. 15459, 1912; abst. J. S. C. I. 1913, **32**, 751; C. A. 1914, **8**, 216; Chem. Ztg. Rep. 1912, **36**, 553. G. Fromont, E. P. 375117. T. Kalinowsky, D. R. P. 265640, 1912; C. A. 1914, **8**, 409; Zts. ang. Chem. 1913, **26**, 691; Chem. Zentr. 1913, **84**, 11, 1630; Zts. Schiess. Spreng. 1913, **8**, 476; Wag. Jahr. 1913, **59**, I, 377. N. Krantz, D. R. P. 288670, 1915; abst. C. A. 1916, **10**, 2505. E. v. Lippmann, Chem. Ztg. 1912, **36**, 437. G. Lüttgen, D. R. P. 244402, 1910; abst. J. S. C. I. 1912, **31**, 384; C. A. 1912, **6**, 2300; Zts. ang. Chem. 1912, **25**, 643; Chem. Zentr. 1912, **83**, I, 958; Chem. Ztg. Rep. 1912, **36**, 202; Wag. Jahr. 1912, **58**, I, 376; Mon. Sci. 1916, **83**, 208. T. Oliver, U. S. P. 1229316, 1917; abst. J. S. C. I. 1917, **36**, 872; Anp. Rep. Soc. Chem. Ind. 1917, **2**, 178. M. Schwab and H. Greene & Sons, E. P. 24619, 1903; abst. J. S. C. I. 1904, **23**, 983. M. Seeck, E. P. 474302, 1914; abst. J. S. C. I. 1915, **34**, 715. R. Winslow and B. Hart, E. P. 26916, 1902; abst. J. S. C. I. 1903, **22**, 1194. S. Barth, Zts. ang. Chem. 1909, **22**, 1937; 1911, **24**, 1446. L. Klippert, Chem. Ztg. 1911, **35**, 649; Zts. ang. Chem. 1911, **24**, 1345. H. Petersen and I. Ising, D. R. P. 218726; abst. Wag. Jahr. 1910, **56**, I, 411. O. Guttmann, J. S. C. I. 1908, **27**, 667. R. Moritz, E. P. 11123, 1909. U. S. P. 981103. E. P. 395694. D. R. P. 235800; Chem. Trade J. 1911, **49**, 493. E. Hartmann Ges., E. P. 17035, 1913. D. R. P. 271926. J. Harris and D. Thomas, E. P. 6026, 1915; abst. J. S. C. I. 1915, **34**, 1249. A. Nemes, E. P. 24223, 1913; abst. J. S. C. I. 1914, **33**, 593. M. Seeck, E. P. 16187, 1914. E. P. 474502. J. Carmichael and F. Guillaume, E. P. 15679, 1913; abst. J. S. C. I. 1914, **33**, 830.
2. E. Hartmann and F. Benker, Zts. ang. Chem. 1906, **19**, 136; abst. Chem. Centr. 1906, **77**, I, 975.
3. A. Burgemeister, Chem. Ztg. 1889, **13**, 1633; abst. Jahr. Chem. 1889, **42**, 2649.

1204); it may be stated that, with the introduction of water-sprays, chambers have been made higher. The use of chambers of special shape will be discussed later. According to O. Guttman,¹ in English practice it is usual to use chambers which are not very long, and taller than they are wide.

The combination of chambers into sets varies in different countries. The total space is almost invariably divided into several chambers, although Scheurer-Kestner² refers to a single chamber of 142,000 cu. ft. capacity, and states that it is quite unnecessary to divide the space among several chambers. The actual mode of division varies considerably.³ Three or more chambers may be coupled in series, or two side branches in series may pass into a single chamber or set of chambers. In France and modern German works, three chambers are usual, in England four chambers are common. Subdivision of chamber space is useful in assisting in the cooling of the gases, but they should not be unduly small, on account of the increased amount of lead required.⁴ In English practice it is usual to allow 0.2 sq. ft. total surface (top, bottom, sides and ends) for every cu. ft. of chamber space.

The chambers are joined by connecting tubes of lead, which pass from the end of one chamber to the opposite end of another, so that no dead space is left, and the gases travel straight through the chambers. Gas should enter the first chamber at the top, beyond this opinions differ, some contending it is preferable to allow the gas to issue from the chamber at the bottom, and enter the next one at the top, while others hold the opposite view. If there is any peculiar advantage in any one system, it is probably that in which the pipes enter and leave the chambers about

1. J. S. C. I. 1903, **22**, 1332. See also C. Grosse-Leege, D. R. P. 162218; abst. Zts. ang. Chem. 1905, **18**, 1909. O. Niedenführ, D. R. P. 189834. L. Fromont, D. R. P. 191723; abst. Chem. Zentr. 1908, **79**, I, 314. E. P. 4861, 1907. F. P. 375117. Belg. P. 190625, 1906. J. Fels, D. R. P. 228696; abst. Chem. Zentr. 1910, **81**, II, 1789. G. Lüttgen, D. R. P. 244402; abst. Wag. Jahr. 1912, **58**, I, 376.

2. A. Wurtz, Dict. Chim. **3**, 147.

3. F. Benker and E. Hartmann, Zts. ang. Chem. 1906, **19**, 137. O. Eliel, U. S. P. 860968. A. Marlow, U. S. P. 882330. R. Hasenclever, Chem. Ind. 1899, **22**, 26. See also G. Lunge, Zts. ang. Chem. 1894, **7**, 133. L. Pierron, Mon. Sci. 1900, **56**, 563. F. Benker, D. R. P. 88368, 91260; abst. Ber. 1896, **29**, 883; Wag. Jahr. 1897, **43**, 423.

4. F. Bode, Zts. ang. Chem. 1890, **3**, 11. A. Schertel, Chem. Ind. 1889, **12**, 80. A. Retter, Zts. ang. Chem. 1891, **4**, 4.

midway in height. The connections are usually round pipes of lead, of 9-12-lb. weight, bound with iron hoops, and wooden staves between these and the lead. The width of the pipe must be adapted to the quantity of gas conveyed; for 7 tons of pyrites daily a 2-ft. pipe is sufficient; for 9 tons, one of 2½-ft.; upwards of this 3-ft. is used, since more than 10 tons are rarely burnt in a single set of chambers.¹

The size of the individual chambers is usually given in cu. ft. per lb. of sulfur burnt as brimstone or pyrites per 24 hours. It is stated that for pyrites more space is required than for brimstone, in the ratio 1:1.314. As to the capacity of the chambers themselves, divergent opinions and practice exist. Generally speaking, the capacity will depend on the supply of niter used, and with the amount of nitrogen oxides in circulation, i. e., with so-called intensive working, the chamber space is less than for ordinary operation of the chambers. For non-intensive working, with pyrites, 16-20 cu. ft. are allowed per lb. of sulfur burnt per 24 hours; with intensive working, 10 cu. ft. may be used. Another factor which influences the capacity is the size of the Glover and Gay-Lussac towers.² If the gases are more efficiently cooled by a good Glover tower, less chamber space is required.

Intensive Working of Chambers. In recent years it has become increasingly the custom to work the chambers on what is called the *intensive system*. In this they are supplied with a stock of circulating nitrogen oxides greatly in excess of what is sufficient for ordinary working. This was first introduced in French factories. In German works the chamber space is cut down to about 14 cu. ft. per lb.; in British practice 10 cu. ft. is common for intensive working. Considerable discussion has arisen on the relative advantages of the old and the intensive systems of working.³ The consumption of niter has been stated

1. E. Höfling, D. R. P. 202631; abst. Chem. Zentr. 1908, **79**, II, 1653. R. Winsloe and B. Hart, E. P. 26916, 1902. H. Hegeler and N. Heinz, U. S. P. 728914, 752377. E. P. 254, 1904. J. Lagache, F. P. 350363. G. and A. Davis, E. P. 20012, 1904. H. Porter, Chem. Trade J. 1909, **44**, 79; J. S. C. I. 1909, **28**, 338. R. Cellarius, D. R. P. 166745, 183097.

2. See C. Wright, Chem. News, 1867, **16**, 94. A. Clement, Wag. Jahr. 1899, **45**, 370. Alkali Inspectors Reports, **20**, 48; **21**, 20.

3. See L. Pierron, Mon. Sci. 1900, **55**, 367. O. Guttman, J. S. C. I. 1903, **22**, 1334. H. Petersen, Zts. ang. Chem. 1907, **20**, 1101; 1911, **24**, 877. A. Nemes, Zts. ang. Chem. 1911, **24**, 387, 1564. F. Hartmann, Zts. ang. Chem. 1911, **24**, 2302. F. Lütty and H. Niedenführ, Zts. ang. Chem. 1902, **15**, 242.

to be higher, and lower, with intensive working, and nothing definite can be asserted. The cost of repairs appears to be higher with intensive working. Lunge¹ in considering this discussion, states that the method is extending, and most modern works seem decidedly in favor of the intensive system.¹⁰

Other proposals for diminishing the chamber space, besides the use of special types of chambers (to be considered later), include: the use of pure oxygen instead of air in the chambers,² mixing apparatus in the chambers,³ and arrangements for cooling.⁴

The Moritz Chambers. In the system patented by R. Moritz⁵ the chamber building is constructed of iron or reinforced concrete, and the roof is proportioned to carry the whole weight of the chambers. The top of the chamber is arched and secured to the roof by iron hangers. Wooden or other supports are thus entirely eliminated, whereby much better cooling is claimed, with consequently less wear and tear on the lead. The chamber walls are similarly suspended so as to allow of expansion without undue buckling. The hangers are attached to straps of lead burnt on to the chamber walls. It is alleged that better cooling, more

F. Lütty. Zts. ang. Chem. 1903, **18**, 1257. W. Hess, Zts. ang. Chem. 1905, **18**, 376. H. Schmidl, Zts. ang. Chem. 1908, **21**, 249. O. Proclss, Chem. Ztg. 1910, **34**, 1322. C. Opl, Zts. ang. Chem. 1909, **22**, 1961. M. Hasen clever, J. S. C. I. 1911, **30**, 1292. See also 47th Official Report on Alkali Works, 1911, 15.

1. G. Lunge, "Sulfuric Acid and Alkali," 4th Ed. **1**, 647.

2. T. Terell, W. Hogg and J. Tomlinson, E. P. 3116, 1871. A. and L. Brin, E. P. 12070, 1886. G. Lunge, E. P. 3117, 1888. A. Schenrer-Kestner, Bull. Soc. Ind. Mulhouse, 1890, 276.

3. O. Eliel, U. S. P. 860968. R. Evers, D. R. P. 151723; abst. Wag. Jahr. 1904, **50**, I, 516. T. Richters, D. R. P. 15252; abst. Wag. Jahr, 1881, **27**, 162. N. Pratt, E. P. 4856, 1895. U. S. P. 652687, 652688, 652689, 652690. E. P. 10757, 1899. O. Guttmann, J. S. C. I. 1903, **22**, 1332. H. Rabe, D. R. P. 237561, 240474. E. Hartmann, Chem. Ztg. 1897, **21**, 877. Ward, E. P. 1006, 1861.

4. F. Blau, D. R. P. 95083. L. Fromont, E. P. 4861, 1907. D. R. P. 191723. K. Walter and E. Boeing, D. R. P. 71908; abst. Ber. 1894, **27**, 175-R. Brulfer, F. P. 220402; abst. Mon. Sci. 1893, **42**, 53. O. Niefenführ, D. R. P. 241894. See H. Bornträger, Chem. Ind. 1885, **8**, 386. J. Mactear, J. S. C. I. 1884, **3**, 228.

5. U. S. P. 981103; abst. J. S. C. I. 1911, **30**, 130; C. A. 1911, **5**, 1173. E. P. 11128, 1909; abst. J. S. C. I. 1910, **29**, 757. E. P. 13175, 1912; abst. C. A. 1913, **7**, 3821; J. S. C. I. 1912, **31**, 1180. F. P. 395694, 444474; abst. J. S. C. I. 1912, **31**, 1124; C. A. 1913, **7**, 1591; Chem. Ztg. Rep. 1913, **37**, 62. Belg. P. 215408, 1909; 256581, 1913. D. R. P. 235800; abst. C. A. 1911, **5**, 3503; Zts. ang. Chem. 1911, **24**, 1446; Chem. Zentr. 1911, **82**, II, 238; Chem. Ztg. Rep. 1911, **35**, 374; Wag. Jahr. 1911, **57**, I, 416; Zts. Schiess. Spreng. 1911, **6**, 334. A detailed description of the Moritz chambers is given by S. Barth, Zts. ang. Chem. 1909, **22**, 1937; abst. C. A. 1910, **4**, 648.

efficient equalization of temperature within the chambers, less solvent action on the lead cheaper and more rapid construction and greater economy of niter result from this system.

The chambers are preferably circular in section or square with rounded corners. Since no wood is used the plant is fire-proof.

Details of plants constructed on this system have been given by Klippert¹ and T. Norton.² The chamber plants erected by the Simon-Carve³ firm are on the Moritz principal. Moritz has also described reaction towers, and rotary pyrites burners.⁴

The Nidenführ Chamber. Nidenführ describes⁵ a lead chamber in which the gases take a spiral course, an arrangement which is claimed to lead to more energetic reaction. Dead spaces in the chamber are eliminated, and as the whole of the space is utilized, it is claimed that a reduction of the chamber capacity results. A circular chamber is employed, in which partitions are following a spiral course. These serve both to impart a vortical motion to the gas and also to collect liquid which condenses in the chamber. The spiral partition may commence from the outer wall, or may be separated from it. The construction is of cylindrical or conical perforated earthenware packing bodies. The entering gas impinges on these bodies, and partly passes through them. The droplets of acid collect inside the bodies and run down to the bottom of the chamber. It has been stated that by the use of this system an output double or treble that obtained in ordinary chambers may be attained.

Falding's Chamber. A new type of sulfuric acid chamber was introduced in 1909 by F. Falding of New York,⁶ who em-

1. Zts. ang. Chem. 1911, **24**, 1345; abst. C. A. 1911, **5**, 3882.
2. Chem. Trade J. **49**, 493. J. Ind. Eng. Chem. 1912, **4**, 532; abst. C. A. 1912, **6**, 795, 2498.
3. Anon., Gas World, Coking and By-Products Sect. 1916, **65**, 14; abst. C. A. 1917, **11**, 386.
4. R. Moritz, F. P. 462877; abst. C. A. 1914, **8**, 3103; Chem. Ztg. Rep. 1914, **38**, 358.
5. F. P. 382990, 1907; abst. J. S. C. I. 1908, **27**, 280. D. R. P. 241894, 1910; abst. C. A. 1912, **6**, 2152; Zts. ang. Chem. 1912, **25**, 137; Chem. Zentr. 1912, **83**, I, 295; Chem. Ztg. Rep. 1912, **36**, 43; Wag. Jahr. 1911, **57**, I, 419; Zts. Schiess. Spreng. 1912, **7**, 55.
6. U. S. P. 932771, 1909; abst. Chem. Ztg. Rep. 1909, **33**, 542; Mon. Sci. 1910, **73**, 82. E. P. 26452, 1909; abst. J. S. C. I. 1910, **29**, 1010. F. P. 410556; abst. Mon. Sci. 1913, **79**, 72. D. R. P. 241509; abst. C. A. 1912, **6**, 2151; Zts. ang. Chem. 1912, **25**, 137; Chem. Zentr. 1912, **83**, I, 171; Chem. Ztg. Rep. 1912, **36**, 8; Wag. Jahr. 1911, **57**, I, 418; Zts. Schiess. Spreng. 1912,

ploy but a single chamber, together with a cooler, but this is much higher, viz., up to 70 ft., than has been used before, and has a horizontal section of 50 x 50 ft. In this tall chamber, convection currents are set up, the reacting gas rises and passes to the top of the chamber while the inert gases fall to the bottom. The reaction can be completed in one chamber, but the exit gas is too hot to pass directly to the Gay-Lussac tower and requires to be forced through a cooler. It also contains an excess of moisture, and must be dried. This cooling and drying plant can, however, be installed much more economically than additional chambers. A saving of about 40% in lead is claimed over ordinary chambers, and the chamber space reduced to about 7 cu. ft. per lb. sulfur per 24 hours, the average niter consumption being given as 4%. The chamber is erected on a slab of reinforced concrete, covered with $\frac{3}{4}$ " smooth asphalt, to receive the bottom of the chamber. The side pillars are of steel, connected by angle-iron horizontal bars, which are fastened to the sides of the chamber by continuous lead strips burnt on the latter. The gases pass through the Glover tower, then to the chamber, then to a small cooling tower, entering at the top in both cases, and finally to a Gay-Lussac tower, the latter and the Glover tower being cooled by water.

At Copper Hill, Tenn., there are 36 Falding chambers in operation,¹ and other smaller installations have been erected which are stated to be operating efficiently.

• **The Mills-Packard Chamber.** W. Mills, C. Packard and E. Packard & Co., of Ipswich, England, employ a chamber shaped like the frustum of a cone or pyramid, and cooled by water flowing over the exterior.² This cooling is preferably performed by a series of perforated pipes surrounding the chamber at different

7, 78. Belg. P. 220823, 1909. See Eng. Min. J. 1909, 441; J. S. C. I. 1909, **23**, 1032; abst. C. A. 1910, **4**, 1225. H. Petersen, Zts. ang. Chem. 1911, **24**, 880, 1811. T. Meyers, Zts. ang. Chem. 1911, **24**, 1520. R. Hoffmann, Chem. Ztg. 1913, **37**, 1271. A. Nemes, Zts. ang. Chem. 1911, **24**, 387; Chimiste, 1911, **2**, 177; abst. C. A. 1911, **5**, 2914. See also Anon., Eng. Min. J. **95**, 318; abst. C. A. 1913, **7**, 1587.

1. F. Falding and W. Cathcart, J. Ind. Eng. Chem. 1913, **5**, 223; abst. C. A. 1913, **7**, 1956; J. S. C. I. 1913, **32**, 360.

2. E. P. 12067, 1913; abst. J. S. C. I. 1914, **33**, 692, E. P. Appl. 872, 1918. E. P. 124852; abst. J. S. C. I. 1919, **38**, 272-A. U. S. P. 1112546; abst. J. S. C. I. 1914, **33**, 1047. U. S. P. 1312741, 1312742; abst. J. S. C. I. 1919, **38**, 720-A; C. A. 1919, **13**, 2576; F. P. 492366.

heights to form a number of cooling zones. The water from each zone flows into a corresponding gutter, which also surrounds the chamber itself and, being attached to the main framework as well as to the chamber, helps to support the latter. In this way the temperature may be kept constant in the different seasons. The gas from the Glover tower divides into four equal parts, which pass into equally spaced inlets to the bottom of the first chamber. The gases leave the chamber from an opening centrally placed at the top, the succeeding chambers being similarly arranged.

The diameter of the chamber is not constant, but diminishes from the bottom upwards, preventing the tendency of the gas to become rarefied as it deposits liquid in the chamber, and also by cooling. Considerable importance is attached to this condition by the inventors.

It is stated that a very large production of acid is obtained, viz., only 3 cu. ft. per lb. of sulfur burnt per 24 hours, as against 10-15 ft. in ordinary chambers. There is economy in lead and floor space, and increased cooling surface.

These chambers have been erected in England at different works, and appear to have given satisfaction.¹

Tangential Chambers. T. Meyer² has devised circular chambers, with inlet pipes adapted tangentially on the upper part of the sides, and the outlet pipe centrally in the bottom. This causes the gases to traverse the chambers in a spiral manner, rapid at the periphery, slower towards the center, so that they cover a greater distance and are better mixed than in an ordinary chamber. By impinging on the cooler walls of the chamber the gases also tend to deposit the sulfuric acid formed, which leads to an acceleration of the reaction in the chamber.

The system was later improved by the inventor³ by combin-

1. See Chem. Trade J. 1915, **57**, 131. See P. Truchot, Ind. Chim. min. met. 1919, **6**, 57; abst. C. A. 1919, **13**, 1621.

2. D. R. P. 226792, 1910; abst. C. A. 1911, **5**, 1501; Zts. ang. Chem. 1910, **23**, 2340; Chem. Zentr. 1910, **81**, II, 1344; Jahr. Chem. 1910, **63**, I, 524; Chem. Ztg. Rep. 1910, **34**, 543; Wag. Jahr. 1910, **56**, I, 406; Mon. Sci. 1912, **77**, 242; Zts. Schiess. Spreng. 1910, **5**, 440. D. R. P. 186164, 1906; abst. J. S. C. I. 1908, **27**, 502; C. A. 1908, **2**, 166; Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 755; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1907, **31**, 324; Wag. Jahr. 1907, **53**, I, 331; Mon. Sci. 1909, **71**, 153. E. P. 18376, 1898; abst. J. S. C. I. 1899, **18**, 494. Belg. P. 137467, 1898; 164791, 1902.

3. T. Meyer, Zts. ang. Chem. 1900, **13**, 742; Chem. Ztg. 1900, **24**, 601; abst. J. S. C. I. 1900, **19**, 823.

ing the first (hottest) chamber with a cooling system, composed of 43 lead pipes 2" to 2 1/2" wide, suspended in water-lutes from the roof and hanging down inside the circumference to a depth of 8-10 ft. T. Meyer¹ also suggests charging these tubes (insulated) alternately, positively and negatively, and using them for electrostatic precipitation of acid fog.

Meyer's chambers have been installed at Harburg, at the Nord-deutsche Chemische Fabrik, and at the Chemische Dünger Fabrik. They are 10 m. diameter and 8 m. high, in a set of three, with Glover and Gay-Lussac towers.

Particulars of production² indicate that what is attained is favorably comparable with good ordinary chamber plants working on the intensive system. O. Guttman³ states that Meyer's tangential chambers have been a success, and A. Nemes states that 39 factories had been erected on this principle up to 1911. The initial cost of plant is rather high on account of the use of iron frames, but there are compensating advantages. Meyer guarantees a production of 11.6 cu. ft. chamber space per lb. sulfur, with a niter consumption of 3%, figures which have been verified by Guttman.⁴

J. Harris and D. Thomas⁵ use a circular chamber with a tangential inlet pipe at the bottom, inside of which is a central hollow column extending upwards from the pan and opening at the upper part in the chamber to form an exit pipe for the gases. The central column may be cooled by sprays of water or weak acid directed against it, or by adjacent water-cooled pipes, and the last chamber of the series may be packed and supplied with acid, thus replacing part of the absorption tower at the end of the system. G. Lüttgen also advocates semi-circular or polygonal roofs and bottoms, the latter being perforated to keep them free from acid. The inlet tube is tangential and placed opposite to

1. Zts. ang. Chem. 1901, **14**, 1245; abst. J. S. C. I. 1902, **21**, 114.

2. Zts. ang. Chem. 1902, **15**, 151. T. Meyer, Chem. Ztg. 1899, **23**, 296; Zts. ang. Chem. 1899, **12**, 656; 1900, **13**, 739; 1904, **17**, 477. Also pamphlet, Das Tangential-Kammersystem, Offenbach, 1904.

3. J. S. C. I. 1903, **22**, 1332. See also Zts. ang. Chem. 1911, **24**, 391.

4. T. Meyer, Zts. ang. Chem. 1904, **17**, 926. W. Hess, Zts. ang. Chem. 1905, **18**, 376. E. Hartmann and F. Benker, Zts. ang. Chem. 1904, **17**, 554. K. Beskow, Zts. ang. Chem. 1908, **21**, 2312; abst. J. S. C. I. 1908, **27**, 1150. A. Nemes, Zts. ang. Chem. 1911, **24**, 392.

5. E. P. 104461, 1916; abst. J. S. C. I. 1917, **36**, 502; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 178.

the outlet tube, which may either be tangential or central.¹

A tangential chamber system is described by L. Thiele.² T. Meyer³ suggests, as an ideal plant, a tangential chamber serving to mix the gases from the burners and separate dust, followed by two Glover towers, one for denitrating and the other for concentrating the acid, then a tangential chamber with coolers, and finally one or two plate-towers to remove mist, before the gases pass the Gay-Lussac tower(s). He is in accord with the most improved practice in recommending ample Gay-Lussac space.

Intermediate Reaction Towers. The space required for the production of acid in the chamber process may be reduced by the introduction of cooling and mixing towers between the chambers, and in some cases the chambers may be entirely dispensed with, and the whole process carried out in the towers.

Reaction towers were proposed by J. Thyss,⁴ and improved by E. Sorel,⁵ but were adapted to practical use by G. Lunge⁶ in collaboration with L. Rohrmann.⁷ These so-called *Lunge towers*, or *plate towers*, have been largely applied in the construction of modern plants by O. Niedenführ⁸ and by F. Lütty.⁹ A different type of reaction tower is that of F. Hacker and P. Gilchrist.¹⁰ Other investigations on the reaction tower have been made by

1. G. Lüttgen, D. R. P. 244402, 1910; abst. C. A. 1912, **6**, 2300; Zts. ang. Chem. 1912, **25**, 643; Chem. Zentr. 1912, **83**, I, 958; Chem. Ztg. Rep. 1912, **36**, 202; Wag. Jahr. 1912, **58**, I, 376; Mon. Sci. 1916, **83**, 208; Zts. Schiess. Spreng. 1912, **7**, 184.

2. U. S. P. 1267012; abst. C. A. 1918, **12**, 1817; J. S. C. I. 1918, **37**, 506-A.

3. Zts. ang. Chem. 1901, **14**, 1245; abst. J. S. C. I. 1902, **21**, 114.

4. D. R. P. 30211; abst. Wag. Jahr. 1885, **31**, 216. E. P. 9317, 1884; abst. J. S. C. I. 1885, **4**, 498. See G. Lunge, Zts. ang. Chem. 1889, **2**, 265, 279. J. Hannay, E. P. 14247, 1886; abst. J. Soc. Dyers Col. 1886, **2**, 210.

5. Bull. Soc. Ind. Mulhouse, 1889, 240; J. S. C. I. 1890, **9**, 175.

6. Zts. ang. Chem. 1889, **2**, 385. E. Hartmann, Zts. ang. Chem. 1911, **24**, 2303. P. Hofmann, Zts. ang. Chem. 1905, **18**, 407.

7. E. P. 10355, 1885; abst. J. S. C. I. 1886, **5**, 468. E. P. 10037, 1886; abst. J. S. C. I. 1887, **6**, 597. E. P. 6989, 1889; abst. J. S. C. I. 1890, **9**, 510. G. Lunge, Ber. 1881, **14**, 2200.

8. D. R. P. 200820, 1906; abst. J. S. C. I. 1908, **27**, 939; Zts. ang. Chem. 1908, **21**, 2041; Chem. Zentr. 1908, **79**, II, 654; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1908, **32**, 452; Wag. Jahr. 1908, **54**, 369; Chem. Zts. 1908, **7**, 974; Zts. Schiess. Spreng. 1908, **3**, 374. See Chem. Ztg. 1897, **21**, 176; 1896, **20**, 31. Zts. ang. Chem. 1900, **13**, 960.

9. Zts. ang. Chem. 1897, **10**, 484; abst. Wag. Jahr. 1897, **43**, 425.

10. E. P. 15895, 1893. U. S. P. 503847, 1893; abst. J. S. C. I. 1893, **12**, 1032; J. A. C. S. 1893, **15**, 476. Cf. also J. S. C. I. 1894, **13**, 1142; 1899, **18**, 461. R. Winsloe and B. Hart, E. P. 20142, 1901; abst. J. S. C. I. 1902, **21**, 1183. B. Hart and G. Bailey, J. S. C. I. 1903, **22**, 473.

H. Rabe,¹ F. Benker,² H. Niedenführ,³ R. Cellarius,⁴ M. Schwab and H. Greene & Sons,⁵ O. Niedenführ,⁶ F. Brandenburg,⁷ A. Wilhelmii,⁸ I. Lihme, and The Graselli Co.,⁹ J. Graham,¹⁰ J. Moscicki,¹¹ J. Broome,¹² E. Hartmann,¹³ H. Petersen,¹⁴ and H. Vollberg.¹⁵ A considerable amount of attention has therefore been

1. Zts. ang. Chem. 1903, **16**, 437; abst. Chem. Centr. 1903, **74**, I, 1446.
2. F. P. 238872; abst. Mon. Sci. 1895, **46**, 57.
3. Chem. Ztg. 1897, **21**, 176. Cf. Chem. Ztg. 1896, **20**, 31; abst. J. S. C. I. 1896, **15**, 541.
4. D. R. P. 166745; abst. Zts. ang. Chem. 1906, **19**, 1942; Chem. Centr. 1906, **77**, I, 420; Jahr. Chem. 1905-1908, I, 1612, 1613; Chem. Ztg. Rep. 1906, **30**, 21; Wag. Jahr. 1905, **51**, I, 395; Chem. Zts. 1906, **5**, 368. E. P. 22080, 1905; abst. J. S. C. I. 1906, **25**, 696. F. P. 360634; abst. Mon. Sci. 1906, **65**, 142. D. R. P. 183097; abst. Zts. ang. Chem. 1908, **21**, 795; Chem. Zentr. 1907, **78**, II, 651; Jahr. Chem. 1905-1908, I, 1613; Chem. Ztg. Rep. 1907, **31**, 168; Wag. Jahr. 1907, **53**, I, 335; Mon. Sci. 1909, **71**, 154; Zts. Schiess. Spreng. 1907, **2**, 194.
5. E. P. 24619, 1903; abst. J. S. C. I. 1904, **23**, 983.
6. D. R. P. 189238; abst. Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 1949; Jahr. Chem. 1905-1908, I, 1251; Chem. Ztg. Rep. 1907, **31**, 549; Wag. Jahr. 1908, **54**, I, 370. D. R. P. 189330; abst. Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 1951; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1907, **31**, 549; Wag. Jahr. 1907, **53**, I, 332; Chem. Zts. 1907, **6**, No. 367; Zts. Schiess. Spreng. 1907, **2**, 435. D. R. P. 189834; abst. Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 1953; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1907, **31**, 586; Wag. Jahr. 1907, **53**, I, 332; Chem. Zts. 1907, **6**, No. 362. D. R. P. 200820; abst. Zts. ang. Chem. 1908, **21**, 2041; Chem. Zentr. 1908, **79**, II, 654; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1908, **32**, 452; Wag. Jahr. 1908, **54**, I, 369; Chem. Zts. 1908, **7**, 974; Zts. Schiess. Spreng. 1908, **3**, 374.
7. E. P. 7116, 1907; abst. J. S. C. I. 1907, **26**, 1272. U. S. P. 859427, 1907; abst. J. S. C. I. 1907, **26**, 862. D. R. P. 189830, 1906; abst. Chem. Zentr. 1907, **78**, II, 1947.
8. D. R. P. 184842; abst. Chem. Ztg. Rep. 1907, **31**, 271.
9. U. S. P. 852390; abst. Chem. Ztg. Rep. 1907, **31**, 255.
10. E. P. 6051, 1902; abst. J. S. C. I. 1903, **22**, 907. E. P. 10814, 1906; abst. J. S. C. I. 1907, **26**, 406.
11. D. R. P. 236385; abst. C. A. 1912, **6**, 1970; Zts. ang. Chem. 1911, **24**, 1534; Chem. Ztg. Rep. 1911, **35**, 442; Wag. Jahr. 1911, **57**, I, 652. D. R. P. 234259; abst. C. A. 1912, **6**, 1825; Zts. ang. Chem. 1911, **24**, 1097; Chem. Zentr. 1911, **82**, I, 1618; Chem. Ztg. Rep. 1911, **35**, 302; Wag. Jahr. 1911, **57**, I, 652.
12. U. S. P. 850517.
13. D. R. P. 282747; abst. Zts. ang. Chem. 1915, **28**, 206; Chem. Zentr. 1915, **86**, I, 715; Chem. Ztg. Rep. 1915, **39**, 114. E. Hartmann and F. Benker, D. R. P. 284636; abst. Zts. ang. Chem. 1915, **28**, 364; Chem. Zentr. 1915, **86**, II, 168; Chem. Ztg. Rep. 1915, **39**, 244; Mon. Sci. 1917, **84**, 77; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110. Cf. Feigensohn, Chem. Ztg. 1906, **30**, 851.
14. E. P. 27738, 1907; abst. J. S. C. I. 1908, **27**, 981. U. S. P. 908696, 1909; abst. J. S. C. I. 1909, **28**, 140; Chem. Ztg. Rep. 1909, **33**, 90; Mon. Sci. 1909, **71**, 116.
15. D. R. P. 265724; abst. C. A. 1914, **8**, 409; Zts. ang. Chem. 1913, **26**, 684; Chem. Zentr. 1913, **84**, II, 1629; Chem. Ztg. Rep. 1913, **37**, 597; Wag. Jahr. 1913, **59**, I, 505.

given to this subject recently by numerous investigators.

According to Lunge the action of the plate towers is chiefly concerned with the retention of the liquid droplets of acid, which are produced in the reaction, and in the ordinary chamber float about in the form of a fine mist, by striking the plates of the tower. The temperature inside the tower is kept from rising too high by a spray of water or dilute sulfuric acid, which is also required in the chamber reactions.

The use of towers for the manufacture of sulfuric acid had been proposed at an early date by W. Gossage,¹ W. Petrie,² M. Adouin and E. Pelouze,³ and A. de Hemptinne.⁴ The credit of bringing these into successful use, however, undoubtedly is to be ascribed to Lunge.

The Lunge tower consisted originally of a column of stoneware cylinders filled with special plates. The later type consists of a lead shell, of circular or rectangular section, packed with stoneware plates supported on bearers in such a way that each plate is independent of the others and rests on the horizontal ledge of its own bearer, the pressure of the superposed plates being taken by the vertical parts of the bearers. Inlet and outlet pipes, acid feed, etc., are provided.

Each plate is covered with a network of small ledges, and in each of the squares so formed is a perforation with a somewhat raised margin. The height of the margin is not quite so great as the ledges, so that a layer of liquid about $\frac{1}{8}$ in. deep remains on the squares, the excess dropping through the perforations. The position of the holes differs in successive plates, so that to each perforation in one plate there corresponds the point of union of the ledges in the plates above and below. In this way the

1. E. P. 107, 1857. E. P. 2569, 1857. E. P. 996, 1856.

2. E. P. 1985, 1860.

3. E. P. 109, 1873.

4. E. P. 2807, 1874. See also R. Heintz, Zts. ang. Chem. 1906, **19**, 705. Chem. Fabr. Griesheim-Elektron, Aust. P. 52178, 52179, 1910. D. R. P. 218779, 1908; abst. C. A. 1910, **4**, 2032. D. R. P. 226610, 1908; abst. C. A. 1911, **5**, 1326. D. R. P. 287784, 1913; abst. C. A. 1916, **10**, 2028. E. P. 23442, 1909; abst. C. A. 1911, **5**, 2706. U. S. P. 1048953, 1912; F. P. 406641, 1909; abst. J. S. C. I. 1910, **29**, 487; 1913, **32**, 142; C. A. 1911, **5**, 1666. Metallbank u. Metallurgische Ges. and H. Klencke, D. R. P. 284995, 1913; abst. J. S. C. I. 1915, **34**, 1091. Maurecourt, Engrais, **26**, 995; abst. C. A. 1912, **6**, 535. E. Hoefling, D. R. P. 281135, 1912; abst. J. S. C. I. 1915, **34**, 611. H. Klencke, E. P. 25027, 1909; abst. C. A. 1911, **5**, 163. F. Curtius & Co., D. R. P. 295708, 1914; abst. J. S. C. I. 1917, **36**, 646. A. Foster, U. S. P. 1277896; abst. C. A. 1918, **12**, 2414.

liquid is prevented from running straight through, but is divided into drops. The absorbing surface consists, therefore, of the thin film of liquid on the plates, and the surface constantly renewed by the scattering of liquid about the plates.

The gases and vapors passing up the tower are divided into a number of jets by the holes in the plates, and the gas leaving one hole impinges on the solid places of the plate above; where small drops are deposited. The direction of flow of the gas is also constantly changed, so that by this motion of liquid and gas, a very intimate contact is attained. It is claimed that in this way a more intimate contact is obtained than in a coke tower. It is stated that a plate tower does ten to twenty times as much work as a coke tower of the same cubic space. If obstruction occurs, the tower is flushed with water.

By flooding the tower with weak acid or water, the temperature is kept down to 70°–80°.

Lunge advises the use of the towers as follows: Since most of the acid is made in the first part of the chamber, the back of the chamber is cut out, leaving only about 50 ft. from the Glover tower, and replaced by a plate tower of sufficient section and containing 40 plates. This will be about 18 ft. high. A smaller chamber, say 30 ft. long, follows the tower, then another plate tower, another small chamber for drying the gases, and at the end a plate tower arranged as a Gay-Lussac tower. The first part of the chamber is retained because there the production of acid goes on very efficiently, i. e., in a comparatively small space. This design has also been adopted by O. Niedenführ,¹ who mentions in addition the possibility of flue dust, and the high temperature interfering with the operation of the tower. The dust problem also prevents towers of this type being substituted for the Glover tower, although a few tiers of plates with 1/2-in. holes may with advantage be placed in the upper part of the Glover. In one works,² the last chamber of a set, having a capacity of

1. D. R. P. 200820, 1906; abst. J. S. C. I. 1908, **27**, 939; Zts. ang. Chem. 1908, **21**, 2041; Chem. Zentr. 1908, **79**, II, 654; Jahr. Chem. 1905–1908, I, 1611; Chem. Ztg. Rep. 1908, **32**, 452; Wag. Jahr. 1908, **54**, 369; Chem. Zts. 1908, **7**, 974; Zts. Schiess. Spreng. 1908, **3**, 374. See Chem. Ztg. 1897, **21**, 176; 1896, **20**, 31. Zts. ang. Chem. 1900, **13**, 960.

2. D. R. P. 200820, 1906; abst. J. S. C. I. 1908, **27**, 939; Zts. ang. Chem. 1908, **21**, 2041; Chem. Zentr. 1908, **79**, II, 654; Jahr. Chem. 1905–1908, I, 1611; Chem. Ztg. Rep. 1908, **32**, 452; Wag. Jahr. 1908, **54**, 369;

38,390 cu. ft. was replaced by a plate tower of 256 plates in 16 layers, without diminishing the production. Each plate made 23.4 lbs. of acid per 24 hours, or about 14 lbs. per cu. ft. of space filled with plates, which is about 100 times the production of chambers.

The horizontal sections of Lunge towers may be taken from the following table:

| S burnt per 24 hours | No. of plates per ton S burnt to replace chambers in different parts of the system | | |
|----------------------|--|--------|------|
| | In front | Middle | Rear |
| Up to 1 ton | 12 | 10 | 6 |
| From 1 to 2½ tons | 12-10 | 10-8 | 6-5 |
| From 2½ to 5 tons | 10-6 | 8-5 | 5-4 |

The number of layers for a given production may be calculated as follows: In the first third of the system, where the plates are at a treble distance from one another ($3 \times 2\frac{1}{2}$ in.), each plate may be assumed to produce in 24 hours 10-12 kgm. H_2SO_4 . In the second layer, at double distance ($2 \times 2\frac{1}{2}$ in.), each plate makes 6-8 kgm., while in the third layer, at single distance ($2\frac{1}{2}$ in.), each plate produces 1.25-2 kgm. acid. Niedenführ proposes to replace the chambers altogether by towers, but this system will be considered under the Opl tower plant (p. 1225).

F. Hacker and P. Gilchrist¹ employ instead of plates, air-cooled lead pipes running horizontally across the tower, and are said to be quite satisfactory. The systems of R. Winsloe and B. Hart, and B. Hart and G. Bailey,² are similar. F. Benker³ replaces Lunge plates by earthenware cylinders. Heinz⁴ proposes Gutt;

Chem. Zts. 1908, **7**, 974; Zts. Schiess. Spreng. 1908, **3**, 374. See Chem. Ztg. 1897, **21**, 176; 1896, **20**, 31. Zts. ang. Chem. 1900, **13**, 960.

1. E. P. 15895, 1893. U. S. P. 503847, 1893; abst. J. S. C. I. 1893, **12**, 1032; J. A. C. S. 1893, **15**, 476. Cf. also J. S. C. I. 1894, **13**, 1142; 1899, **18**, 461. R. Winsloe and B. Hart, E. P. 20142, 1901; abst. J. S. C. I. 1902, **21**, 1183. B. Hart and G. Bailey, J. S. C. I. 1903, **22**, 473.

2. E. P. 15895, 1893. U. S. P. 503847, 1893; abst. J. S. C. I. 1893, **12**, 1032; J. A. C. S. 1893, **15**, 476. Cf. also J. S. C. I. 1894, **13**, 1142; 1899, **18**, 461. R. Winsloe and B. Hart, E. P. 20142, 1901; abst. J. S. C. I. 1902, **21**, 1183. B. Hart and G. Bailey, J. S. C. I. 1903, **22**, 473.

3. F. P. 238872; abst. Mon. Sci. 1895, **46**, 57.

4. E. P. 2807, 1874. See also R. Heintz, Zts. ang. Chem. 1906, **19**, 705. Chem. Fabr. Griesheim-Elektron, Aust. P. 52178, 52179, 1910. D. R. P. 218779, 1908; abst. C. A. 1910, **4**, 2032. D. R. P. 226610, 1908; abst. C. A. 1911, **5**, 1326. D. R. P. 287784, 1913; abst. C. A. 1916, **10**, 2028. E. P. 23442, 1909; abst. C. A. 1911, **5**, 2706. U. S. P. 1048953, 1912; F. P. 406641, 1909; abst. J. S. C. I. 1910, **29**, 487; 1913, **32**, 142; C. A. 1911, **5**, 1666. Metallbank u. Metallurgische Ges. and H. Klencke, D. R. P. 284995, 1913; abst. J. S. C. I. 1915, **34**, 1091. Maurecourt, Engrais, **26**, 995; abst.

mann balls as packing. H. Petersen¹ uses a system of towers and chambers, (1) a Glover tower fed with nitrous vitriol of 60° Bé. and dilute acid; (2) denitrating tower fed with nitrous vitriol of 54°-55° Bé. coming from the Gay-Lussac towers of the second system; (3) lead chambers; (4) Gay-Lussac towers fed with Glover acid of 54°-55° Bé. of the second system; (5) Gay-Lussac towers of the second system fed with 60° Bé. Glover acid. This system of Glover and Gay-Lussac towers is therefore fed with nitrous vitriol of 54°-55° Bé. and weaker acid, while the ordinary Glover and Gay-Lussac towers of the first system are fed with 60° Bé. nitrous vitriol and dilute acid.

Replacement of the Lead Chamber by Other Apparatus.

Numerous proposals have been made for replacing the chambers by other apparatus. A. MacDougal and H. Rawson,² and L. Verstraet and C. Schmidt³ used Woulfe's bottles. Packed and unpacked towers of various shapes and materials have been proposed by W. Hunt,⁴ J. Hannay,⁵ E. Barbier,⁶ A. Staub,⁷ M. Neumann,⁸ G. Schliebs,⁹ R. Heinz,¹⁰ A. Burkhardt,¹¹ Metallbank C. A. 1912, **6**, 535. E. Hoefling, D. R. P. 281135, 1912; abst. J. S. C. I. 1915, **34**, 611. H. Klencke, E. P. 25027, 1909; abst. C. A. 1911, **5**, 163. F. Curtius & Co., D. R. P. 295708, 1914; abst. J. S. C. I. 1917, **36**, 646. A. Foster, U. S. P. 1277896; abst. C. A. 1918, **12**, 2414.

1. E. P. 27738, 1907; abst. J. S. C. I. 1908, **27**, 981. U. S. P. 908696, 1909; abst. J. S. C. I. 1909, **28**, 140; Chem. Ztg. Rep. 1909, **33**, 90; Mon. Sci. 1909, **71**, 116.

2. E. P. 12333, 1848.

3. Bull. Soc. d'Encouragement, 1865, 531; abst. Dingl. Poly. 1866, **179**, 63; Wag. Jahr. 1865, **11**, 226. E. P. 611, 1863. See also L. Chandor, U. S. P. 42985, 1864.

4. E. P. 1919, 1853.

5. E. P. 14247, 1886; abst. J. Soc. Dyers Col. 1886, **2**, 210; J. S. C. I. 1887, **6**, 729.

6. E. P. 12726, 1892; abst. J. S. C. I. 1893, **12**, 602. D. R. P. 69501; abst. Zts. ang. Chem. 1893, **6**, 462; Wag. Jahr. 1893, **39**, 375; Ber. 1893, **26**, 843. See also E. Candiani, Chem. Ind. 1895, **18**, 153. P. de Boissieu, Bull. Soc. Chim. 1894, (3), **11**, 726.

7. E. P. 12675, 1894; abst. J. S. C. I. 1895, **14**, 572. D. R. P. 88784; abst. Ber. 1896, **29**, 925-R. Swiss P. 12965, 1896. See E. Hartmann, Zts. ang. Chem. 1911, **24**, 2303.

8. D. R. P. 169729; abst. Zts. ang. Chem. 1907, **20**, 974; Chem. Centr. 1906, **77**, I, 1637; Jahr. Chem. 1905-1908, I, 1610; Chem. Ztg. Rep. 1906, **30**, 425; Wag. Jahr. 1906, **52**, I, 380; Mon. Sci. 1907, **67**, 146; Zts. Schiess. Spreng. 1906, **1**, 141.

9. U. S. P. 1151294; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111. D. R. P. 287589; abst. Zts. ang. Chem. 1915, **28**, 582; Chem. Zentr. 1915, **86**, II, 861; Chem. Ztg. Rep. 1915, **39**, 446. Belg. P. 261449, 1903.

10. D. R. P. 264640; abst. C. A. 1914, **8**, 219; Zts. ang. Chem. 1913, **26**, 632; Chem. Zentr. 1913, **84**, II, 1436; Chem. Ztg. Rep. 1913, **37**, 553; Wag. Jahr. 1913, **59**, I, 379; Zts. Schiess. Spreng. 1913, **8**, 417.

11. E. P. 29568, 1912; abst. C. A. 1914, **8**, 2040; J. S. C. I. 1913, **32**,

- und Metallurgische Gesellschaft A. G. and H. Klencke,¹ Z. Littmann,² U. Wedge,³ A. Düron,⁴ J. F. Carmichael and F. Guillaume,⁵ F. Curtius and Co.,⁶ R. Bithell and J. A. Beck.⁷ Proposals to use horizontal flues have been made by W. Petrie,⁸ N. Heinz and M. Chase,⁹ E. W. Kauffmann,¹⁰ J. Fels,¹¹ and O. Wentzki.¹² Tanks have been proposed by J. Persoz,¹³ Durand, Huguenin and Co.,¹⁴ and H. Petersen.¹⁵ The reaction of the gases
1109. D. R. P. 259576; abst. C. A. 1913, **7**, 3205; Zts. ang. Chem. 1913, **26**, 348; Chem. Zentr. 1913, **84**, I, 1903; Chem. Ztg. Rep. 1913, **37**, 300; Wag. Jahr. 1913, **59**, I, 374. F. P. 452682; abst. Mon. Sci. 1914, **81**, 9.
 1. D. R. P. 284995; abst. Zts. ang. Chem. 1915, **28**, 364; Chem. Zentr. 1915, **86**, II, 215; Chem. Ztg. Rep. 1915, **39**, 253; Mon. Sci. 1917, **84**, 77; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111.
 2. D. R. P. 281005; abst. Zts. ang. Chem. 1915, **28**, 82; Chem. Zentr. 1915, **86**, I, 176; Chem. Ztg. Rep. 1915, **39**, 1.
 3. U. S. P. 1104590; abst. C. A. 1914, **8**, 3102; Chem. Ztg. Rep. 1915, **39**, 114; Mon. Sci. 1914, **81**, 178.
 4. E. P. 2408, 1913; abst. C. A. 1914, **8**, 2606; J. S. C. I. 1913, **32**, 791. D. R. P. 267138; abst. C. A. 1914, **8**, 795; Chem. Zentr. 1913, **84**, II, 2013; Chem. Ztg. Rep. 1913, **37**, 674; Wag. Jahr. 1913, **59**, I, 379. F. P. 453733; abst. C. A. 1913, **7**, 3645; Chem. Ztg. Rep. 1913, **37**, 474. Aust. P. Ann. A-823, 1913. Belg. P. 253251, 1913.
 5. E. P. 15679, 1913; abst. C. A. 1915, **9**, 132; J. S. C. I. 1914, **33**, 830.
 6. E. P. 28550, 1913. Belg. P. 262545, 1913; abst. J. S. C. I. 1915, **34**, 904; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110. D. R. P. 287784; abst. Zts. ang. Chem. 1915, **28**, 582; Chem. Zentr. 1915, **86**, II, 931; Chem. Ztg. Rep. 1915, **39**, 420.
 7. E. P. 28743, 1913; abst. J. S. C. I. 1915, **34**, 226; Zts. ang. Chem. 1910, **29**, 115; Chem. Ztg. Rep. 1915, **39**, 297; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110.
 8. E. P. 1985, 1860.
 9. U. S. P. 875909; abst. Chem. Ztg. Rep. 1908, **32**, 94; Mon. Sci. 1908, **69**, 51.
 10. D. R. P. 226219; abst. C. A. 1911, **5**, 1326; Zts. ang. Chem. 1910, **23**, 2294; Chem. Zentr. 1910, **81**, II, 1254; Jahr. Chem. 1910, **63**, 624; Chem. Ztg. Rep. 1910, **34**, 527; Wag. Jahr. 1910, **56**, I, 413; Mon. Sci. 1914, **81**, 87.
 11. D. R. P. 228696; abst. C. A. 1911, **5**, 2161; Zts. ang. Chem. 1911, **24**, 88; Chem. Zentr. 1910, **81**, II, 1789; Jahr. Chem. 1910, **63**, I, 523; Chem. Ztg. Rep. 1910, **34**, 632; Wag. Jahr. 1910, **56**, I, 405; Zts. Schiess. Spreng. 1910, **5**, 481.
 12. D. R. P. 230534; abst. C. A. 1911, **5**, 2707; Zts. ang. Chem. 1911, **24**, 427; Chem. Zentr. 1911, **82**, I, 521; Chem. Ztg. Rep. 1911, **35**, 95; Wag. Jahr. 1911, **57**, I, 416; Mon. Sci. 1914, **81**, 84; Zts. Schiess. Spreng. 1911, **6**, 96. D. R. P. 238960; abst. C. A. 1912, **6**, 1971; Zts. ang. Chem. 1911, **24**, 2182; Chem. Zentr. 1911, **82**, II, 1392; Chem. Ztg. Rep. 1911, **35**, 529; Wag. Jahr. 1911, **57**, I, 417; Zts. Schiess. Spreng. 1911, **6**, 410. See Zts. ang. Chem. 1911, **24**, 2440. J. Graham, E. P. 6051, 1902; abst. J. S. C. I. 1903, **22**, 907. U. S. P. 736087, 1903; abst. J. S. C. I. 1903, **22**, 995; J. A. C. S. 1904, **26R**, 183. J. Mackenzie, E. P. 19084, 1913; abst. J. S. C. I. 1914, **33**, 483.
 13. Technologiste, 1856, **17**, 461; Dingl. Poly. 1856, **139**, 427; abst. Wag. Jahr. 1856, **2**, 54.
 14. F. P. 205589, 1890; abst. Mon. Sci. 1891, **38**, 450.
 15. E. P. 15406, 1907; abst. J. S. C. I. 1908, **27**, 796. E. P. 21346, 1907; abst. J. S. C. I. 1908, **27**, 932. E. P. 27738, 1907; abst. J. S. C. I. 1908, **27**, 981. U. S. P. 899898, 899899; abst. Chem. Ztg. Rep. 1908, **32**,

under pressure has been investigated by M. Finch and W. and S. Willoughby,¹ W. Burns,² and J. Herreshoff.³

A tower system has been described by the Chemische Fabrik Griesheim,⁴ in which the chambers are entirely replaced by towers, care being taken that all the sulfur dioxide has been oxidized before the gases pass into the niter recovery system, and that time is allowed for the oxidation of the nitrogen oxides. Sufficient space must be allowed for the gases to remain in the niter recovery apparatus for four minutes. The burner gas passes first through a Glover tower and then to oxidizing towers fed with nitric acid of 30°–35° Bé., where the sulfur dioxide is almost instantaneously oxidized. These towers yield an acid containing 50%–54% H₂SO₄ and about 1% HNO₃, which is passed back to the Glover tower for denitration and concentration. The gases next pass through several towers fed with mixtures of nitric and sulfuric acid of various concentrations, where nitric acid is recovered. A temperature of 35°–65° is prescribed. The total space is 200 cu. m. for 10 tons pyrites per day, 30 cu. m. for oxidation of sulfur dioxide and 170 for recovery of nitric acid. The process has been operated at Griesheim, the following advantages being claimed: the composition of the burner gas may vary within wide limits; acids of higher concentration are obtained than in the chamber process, and the nitric acid is recovered as such. It is doubtful whether the recovery of the nitric acid separately is an advantage, since the rate of oxidation of nitric oxide is slower

592. U. S. P. 904147; abst. Chem. Ztg. Rep. 1909, **33**, 27; Mon. Sci. 1909, **71**, 140. F. P. 378454, 382262. See also Chem. Ztg. 1911, **35**, 493; abst. J. S. C. I. 1911, **30**, 681.

1. E. P. 3086, 1884; abst. J. S. C. I. 1885, **4**, 210.

2. E. P. 14441, 1886; abst. J. S. C. I. 1887, **6**, 662; Chem. Centr. 1888, **59**, 27.

3. U. S. P. 335699, 1886; abst. Wag. Jahr. 1886, **32**, 262; J. A. C. S. 1886, **8**, 66.

4. D. R. P. 226610; abst. C. A. 1911, **5**, 1326; Zts. ang. Chem. 1910, **23**, 2340; Chem. Zentr. 1910, **81**, II, 1255; Jahr. Chem. 1910, **63**, I, 524; Chem. Ztg. Rep. 1910, **34**, 527; Wag. Jahr. 1910, **56**, I, 415; Mon. Sci. 1914, **81**, 86. D. R. P. 229565; abst. C. A. 1911, **5**, 2535; Zts. ang. Chem. 1911, **24**, 133; Chem. Zentr. 1911, **82**, I, 272; Chem. Ztg. Rep. 1911, **35**, 11; Mon. Sci. 1914, **81**, 84. E. P. 20401, 1909; abst. J. S. C. I. 1910, **29**, 1205. E. P. 23442, 1909; abst. J. S. C. I. 1910, **29**, 1307; Chem. Ztg. Rep. 1910, **34**, 632; Mon. Sci. 1914, **81**, 83. Belg. P. 218994, 219727. F. P. 406641 and additions thereto; abst. C. A. 1911, **5**, 1666; Mon. Sci. 1910, **73**, 174. Ital. P. 20774, 25381. Swed. P. 29088, 30825. Span. P. 46267, 46459. Aust. P. 17739. Applications for patents have also been made in the U. S. A. and in Russia. See also F. Guillaume, Belg. P. 185739, 1905.

in presence of air alone than if sulfur dioxide is also present and can be oxidized.¹

The Opl System. A system of towers for the manufacture of sulfuric acid has been adopted by C. Opl, working in conjunction with the Erste Oesterreicher Sodafabrik at Hruschau.² Six towers are used, the first three forming sulfuric acid as Glover towers, and the latter three retaining nitrous gases in the manner of Gay-Lussac towers, and fed with strong acid. The gas leaving the last tower, containing 6% oxygen and 1.5 gm. SO_3 per cu. m. is forced by a fan through coke scrubbers, where the last traces of SO_3 are absorbed. The water required for the formation of acid is supplied only to the second, third and fourth towers, and fresh nitric acid only in the second tower. The acid is moved by emulseurs, that flowing from the last tower being fed to the first, or Glover tower, for denitration and concentration. Acid from the fifth tower goes to the second tower, and that from the fourth tower to the third. All acids pass finally through the first tower, and then to coolers. The acids supplied to the last three towers are cooled.

Owing to better utilization of space, the formation of acid takes place in about 20 minutes instead of four to six hours in the chambers, and the reaction space is only about one-tenth that of chambers. For daily production of 18 tons of 60° Bé. acid, six towers 3 m. square and 12 m. high are necessary. This requires 12 tons pyrites, 4 k. w. power, 4000 cu. m. air compressed to 2 atm., 160 kgm. nitric acid of 36° Bé., 300 cu. m. cooling water, and three men per shift. The cost of erection is

1. A. Hutin, *Rev. prod. chim.* 1918, **21**, 250, 275; abst. C. A. 1919, **13**, 249, 2664. Steuber & Co., D. R. G. M. 541504. W. Waggaman, *Bull.* 283, U. S. Dept. Agric., 1915; abst. J. S. C. I. 1916, **35**, 42; Eng. Min. J. 1916, **101**, 10. U. S. P. 1185029; abst. J. S. C. I. 1916, **35**, 736; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 177. See also K. Quinan, E. P. 130712, 1918; abst. C. A. 1920, **14**, 209.
2. E. P. 20171, 1908; abst. J. S. C. I. 1909, **28**, 657. F. P. 394739; abst. Mon. Sci. 1909, **71**, 136. D. R. P. 217036; abst. C. A. 1910, **4**, 1091; Zts. ang. Chem. 1910, **23**, 382; Chem. Zentr. 1910, **81**, 1, 306; Jahr. Chem. 1909, **62**, I, 488; Chem. Ztg. Rep. 1910, **34**, 63; Wag. Jahr. 1909, **55**, I, 335; Mon. Sci. 1913, **79**, 157; Zts. Schiess. Spreng. 1910, **5**, 52. U. S. P. 1012421; abst. C. A. 1912, **6**, 536; Mon. Sci. 1912, **77**, 130. In this connection see E. Hartmann, Zts. ang. Chem. 1911, **24**, 2302; abst. C. A. 1912, **6**, 795; J. S. C. I. 1911, **30**, 1449. C. Opl, Chem. Ind. 1914, **37**, 523. A. Nemes, Zts. ang. Chem. 1911, **24**, 391. Anon., Chem. Trade J., **52**, 96; abst. C. A. 1913, **7**, 1956.

comparatively speaking, considerably less than that of chambers.

According to Huntington, Heberlein & Co., 30 systems were at work or in course of erection in 1914, and the English Alkali Inspector reported favorably on the system in English works.¹ Criticisms of the process have been advanced by H. Petersen² and T. Meyer,³ and been replied to by E. Hartmann.⁴ Reports of the operation of the system are satisfactory, and it appears to be based on sound principles.

Chamber Fittings. The auxiliary apparatus required for the chamber plant includes arrangements for introducing the niter, the air and the steam or water-spray, as well as a number of smaller fittings required for drawing off the acid and for the control of the process. The latter are usually called *chamber fittings*, and will be described at this stage.

The acid is never drawn off from the chambers by cocks, which would soon be choked by lead sulfate, but by constant level apparatus. A round or square lead box is placed on the staging near the chamber, and connected with the dish at the bottom of the chamber by a wide pipe. Alternatively, the box may be burnt on the chamber. The acid from the box escapes through a valve, comprizing a seat of regulus metal, conical plug of the same material with a wooden handle, and a run-off pipe which is burnt to the valve seat. An alternative is to use a lead siphon with cups at each end to keep it always full of liquid, the second end dipping into the run-off pipe.

A more complicated arrangement, which gives satisfactory results, consists of a siphon rigidly attached to the box and a cylinder surrounding the outer limb of the siphon is suspended so that it may be moved up and down by chain and pulley. According as the level of acid is lower or equal to that in the box, acid will or will not flow from the siphon.

The quality of the acid inside the chamber is ascertained by means of *acid dishes*, *acid drips* or *tell-tales* placed in the interior in suitable positions, and communicating with the outside. For instance, the lead vessel may be burnt inside the chamber about 3 ft. from the bottom, when the acid from it will pass out by a

1. Eng. Alkali Insp. Rep. for 1911; abst. J. S. C. I. 1912, **31**, 716.

2. Zts. ang. Chem. 1912, **25**, 762; abst. J. S. C. I. 1912, **31**, 487.

3. Zts. ang. Chem. 1912, **25**, 203; abst. C. A. 1913, **7**, 1956.

4. Zts. ang. Chem. 1912, **25**, 817; abst. C. A. 1912, **6**, 2295.

tube into a lead cylinder containing a hydrometer. A constant overflow of acid will take place by means of the arrangement of a feeding tube. Simple S-shaped pipes, or flat dishes placed on the chamber floor, and communicating by lead pipes with the outside, may also be used. The drip pipes attached to the chamber walls usually indicate 6° to 10° Tw. less than inner drips, on account of the increased condensation of aqueous vapor on the walls by cooling.¹

Small manholes, luted with moist clay, may be provided on the side of the chamber near the bottom for the purpose of withdrawing samples of the bottom acid, and, if large, for inspection of the inside of the chamber. The sample is taken by a lead or glass dipper, and it must be remembered that differences usually exist between different layers of the acid on the bottom.

The temperatures of the chambers is taken by bent-stem thermometers with the bulbs inside, attached at different points. In order to obviate the possibility of penetrating the chamber lead by mercury in case of breakage, it has been proposed to employ alcohol thermometers.

The pressure in the chamber is indicated by the usual glass pressure gauges fitted through rubber stoppers into the chambers. On the tops small manholes with hydraulic lutes carrying bell-jars, are placed so as to show the color of the gases. The pressure may also be gauged by lifting these. Jars may also be placed on short special branch pipes on the sides of the chambers, and are useful for the inspection of the gases. The height of acid in the chamber bottom is registered by a dipping rod, or by glass floats.²

The Supply of Niter to the Chambers. The nitrogen oxides required to equalize the losses in the catalytic process are supplied to the chamber in different ways: (1) as nitric acid obtained in the gaseous state by the decomposition of sodium nitrate and sulfuric acid in pots placed in the flue passing from the pyrites burners to the Glover tower—the so-called “potting process;” (2) the introduction of ready-made liquid nitric acid to the Glover tower; (3) the introduction of gaseous nitrogen oxides

1. W. Firman and A. Cocksedge, *E. P.* 52, 1909; abst. *J. S. C. I.* 1909, **28**, 707.

2. C. Davidson, *Chem. News*, 1903, **87**, 205; abst. *J. S. C. I.* 1903, **22**, 625.

(NO, N₂O₃, NO₂), produced in special apparatus by the oxidation of ammonia, to the Glover tower or chambers. The last method is comparatively new, but has been employed with great success in several works.

The advantages claimed for the old potting process, which is still extensively employed, are as follows: The chambers are not exposed to possible damage from liquid nitric acid, and its handling is avoided; the preparation of liquid nitric acid, which requires a separate plant, is obviated; the irregular evolution of nitric acid from the pots can be more or less compensated by using several sets of pots and charging them in succession.

The advantages claimed for the use of liquid acid are greater economy (although the contrary is sometimes alleged); the greater regularity and more uniform control assured by admitting liquid acid in a measured stream; avoiding the introduction of false-air into the chambers and escape of chamber gases via the potting apparatus; the possibility of altering the proportion of nitric acid supplied within wide limits at short notice; and economy of sulfuric acid, since less is required in making nitric acid in stills than in the niter pots.

The general conclusion is probably that the potting system and the use of nitric acid are of approximately equal efficiency, but both are being superseded by the new process of introducing gaseous nitrogen oxides from the oxidation of ammonia.¹

Niter pots are placed in an enlargement of the flue from the burners, known as the niter oven, provided with the necessary working doors, and a cast-iron saucer for collecting overflows from the pots. The pots vary in shape: one type is made of cast iron, with ledge at the bottom to facilitate introduction and removal of the pot, and holds 8-12 lbs. of niter. A better type of apparatus consists of a fixed semi-circular, cast iron pot, with cast-iron tube bored conically. This tube projects from the niter oven and serves to run off the fused sodium bisulfate formed by the action of sulfuric acid on sodium nitrate in the pot: $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$, an internal saucer receiving the overflow from the pot. The niter, preferably dried, is introduced through a

1. "The Oxidation of Ammonia Applied to Vitriol Chamber Plants," Official Publication of H. M. Ministry of Munitions, Inventions Department, 1919; London. "Catalysis in Theory and Practice," by E. Rideal and H. Taylor, London, 1919.

closed hopper provided with a damper. The sulfuric acid from a small tank is run in by an S-shaped tube, the acid delivering into this from a siphon with stopcock. The acid is run in slowly, for gradual decomposition of the niter, the apparatus holding 56 lbs. NaNO_3 , and requiring two hours for conversion. Two or more sets of pots are provided, so that they may be charged in turn.

Modifications of the potting system have been described by J. Rice,¹ A. O'Brien,² the Soc. anon. I. Vogel,³ N. Pozzati,⁴ P. Derrig,⁵ H. Howard,⁶ W. Weldon,⁷ J. D. Darling,⁸ R. Vetterlein,⁹ the Soc. Anon. Le Nitrogene,¹⁰ and others.¹¹

R. Macadam and H. Walker¹² spray a solution of niter into a small lead tower traversed by the burner gas, or directly into the chambers. This method has been used with success in plants intended for the manufacture of superphosphates, when the presence of sodium sulfate in the chamber acid is immaterial.¹³ The process had been proposed by J. Potut¹⁴ in 1901.

The methods for the introduction of liquid nitric acid into the chamber system aim at a careful regulation of the supply of acid. This may be effected by means of a Marriotte's stoneware bottle, closed by a rubber stopper and supporting a glass tube pass-

1. E. P. 16757, 1892; abst. J. S. C. I. 1893, **12**, 833. See also N. Heinz, U. S. P. 1315834, 1919; abst. J. S. C. I. 1919, **38**, 818-A.

2. U. S. P. 694024, 1902; abst. J. S. C. I. 1902, **21**, 408.

3. E. P. 6846, 1904; abst. J. S. C. I. 1904, **23**, 1088. D. R. P. 171088; abst. Zts. ang. Chem. 1907, **20**, 974; Chem. Centr. 1906, **77**, 11, 186; Jahr. Chem. 1905-1908, I, 1610; Chem. Ztg. 1906, **30**, 612; Wag. Jahr. 1906, **52**, I, 383; Chem. Zts. 1907, **6**, 20; Zts. Schiess Spreng. 1906, **1**, 221.

4. E. P. 404708, 1909. See also A. Fairlie, Chem. Trade J. 1919, **65**, 384; abst. C. A. 1920, **14**, 451.

5. U. S. P. 850820; abst. Chem. Ztg. Rep. 1907, **31**, 242; Mon. Sci. 1907, **67**, 153.

6. U. S. P. 1151103; abst. C. A. 1915, **34**, 2798; J. S. C. I. 1915, **34**, 1009; Mon. Sci. 1903, **59**, 36.

7. E. P. 1752, 1882; abst. Wag. Jahr. 1882, **28**, 299.

8. E. P. 13171, 1895; abst. Mon. Sci. 1896, **48**, 82.

9. D. R. P. 303557, 1916; abst. J. S. C. I. 1918, **37**, 370-A; Chem. Zentr. 1918, **89**, I, 497; Chem. Ztg. Rep. 1918, **42**, 72.

10. E. P. 404071, 1909; abst. C. A. 1911, **5**, 1664; Chem. Ztg. Rep. 1910, **34**, 18; Mon. Sci. 1910, **73**, 169. Swiss P. 44223, 1908.

11. See Chem. News, 1878, **37**, 155, 194, 203, 216. N. Heinz, U. S. P. 1315834; abst. C. A. 1919, **13**, 2982.

12. E. P. 103877, 1916; abst. C. A. 1917, **11**, 1889; J. S. C. I. 1917, **36**, 385; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 178. Cf. C. Burnard, E. P. 2873, 1875. H. Deacon, E. P. 4348, 1875.

13. Alkali Inspectors Rep. 1913, **50**, 133.

14. E. P. 7710, 1901. Belg. P. 148290, 152676, 1900; abst. J. S. C. I. 1902, **21**, 706.

ing about half-way inside the bottle. Through this tube the air enters, the volume of entering air being equal to that of the acid flowing out. As the height of acid diminishes, the outflow tends to be reduced, but the air enters more freely; in consequence of the shorter liquid column through which it must pass, so that the outflow is more or less constant throughout. The bottle is filled from the top through a funnel, the stopper being raised during the process. The acid passes from the bottle through the funnel to a glass or stoneware pipe, and thence to the chamber system (e. g., to the Glover tower).

Another form of bottle, which minimizes the danger of the only partially opened stopcock being choked with sludge from the acid, is that described by F. Bode.¹ In this method the cock at the bottom is kept wide open, and the rate of outflow regulated by a cock on the tube passing inside the bottle.

The acid may be supplied intermittently by means of a siphon jet, connected with a vessel into which nitric acid is delivered from a container, such as a stoneware bottle with a tap below.

Formerly, the liquid acid was delivered into the chambers themselves, being distributed on stoneware cascades, or sprayed by air.² These methods are now quite obsolete, the acid being always supplied to the Glover tower,³ and is run down the tower together with the nitrous vitriol from the Gay-Lussac tower (see the latter). J. Potut.⁴ and J. Lüttgens,⁵ describe special arrangements for regulating the acid feed.

The liquid nitric acid is stored on the top of the chambers, in large stoneware jars, or in a number of glass carboys connected by glass siphons. F. Pohl⁶ employs iron vessels lined inside with paraffined asbestos cloth. Tanks of stone cemented with a mixture of water glass, asbestos powder and a little barium sulfate, may also be employed. Lead resists the action of strong nitric

1. Dingl. Poly. 1876, **220**, 538. See also M. Liebig, Zts. chem. Grossgew. 1878, part 2.

2. M. Liebig, Zts. Verein deut. Ing. 1879, 111. See J. Parent, F. P. 449035, 1912; abst. Mon. Sci. 1914, **81**, 4. See also A. Burgemeister, Dingl. Poly. 1880, **235**, 277; abst. Wag. Jahr. 1880, **26**, 228.

3. G. Lunge, "Sulfuric Acid and Alkali," 4th Ed. 713. Sorrel, "Fabrication de l'acide sulfurique," 1887, 204. Cf. E. Hartmann and F. Benker, Zts. ang. Chem. 1906, **19**, 135.

4. E. P. 4272, 1900; abst. J. S. C. I. 1901, **20**, 363.

5. E. P. 6617, 1914; abst. J. S. C. I. 1914, **33**, 830.

6. D. R. P. 30188; abst. Tech. Chem. Jahr. 1884, **7**, 520.

acid very well, and a good quality of enameled iron may also be used. G. Adamson¹ describes glass, wax or other bottles, the sides and bottoms being strengthened with wire gauze embedded in the material.²

The use of nitrogen oxides directly introduced into the chambers or into the Glover tower, appears to be the most rational method. In some cases waste gases from other manufacturing processes, such as the preparation of arsenic acid or ferric sulfate may be used, but such sources of supply, although they may be convenient ways of usefully disposing of nitrous gases, will not usually be regular enough or sufficient for use in the vitriol plant. The most successful method is to generate the nitrous gases continuously by the oxidation of ammonia.³

Apparatus for this purpose has been described by Schupphaus,⁴ and by J. Partington. The apparatus recommended by the latter consists of a top and bottom cone, with rectangular body pieces between, all in cast aluminium $\frac{1}{8}$ in. thick. Three body pieces are recommended, but later experiments indicate that two, or even one, will suffice. The area inside is 4 in. by 6 in., the pieces being provided with flanges, $\frac{3}{4}$ in. wide, to facilitate bolting together, perforated baffles of sheet aluminium being inserted between the body pieces, except at the junction between the top cone and body piece, which is occupied by a special catalyst of two layers of platinum gauze, of pure platinum wire 0.0025 in. diam., woven in uniform mesh with 80 strands to the linear inch.

The air and ammonia gas mixture passing through the converter, in the proportion of about 1 vol. NH_3 to 7.5 vols. air, is prepared most conveniently by blowing filtered air through 25% purified ammonia liquor in a coke tower, and driving off the ammonia by admitting a little steam at the base of the tower.

Before entering the converter, the gases must be filtered, as traces of iron oxide, present in dust, poison the platinum.

The reaction is initiated by heating the gauzes electrically.

1. U. S. P. 846541.

2. C. Burnard, E. P. Aug. 14, 1875; see Chem. News, 1878, **37**, 203.

3. G. Taylor and E. Scott (E. P. 127047; abst. J. S. C. I. 1919, **38**, 499-A; C. A. 1919, **13**, 2421) use oxides produced by passing air through an electric arc or Kilburn-Scott furnace.

4. See J. Blinkhorn, E. P. 1084, 1878; abst. J. A. C. S. 1879, **1**, 175; Chem. Ind. 1878, **1**, 384; Wag. Jahr. 1879, **25**, 287.

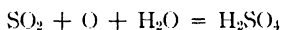
or by heating them with a Bunsen torch inserted beneath the catalyst. When reaction begins, it continues uninterruptedly without external heating. It is desirable to take out the platinum gauzes about once every two months, and clean them by boiling in concentrated hydrochloric acid.

The output per square foot of catalyst surface (two gauzes) is equivalent to 1.8 tons of HNO_3 per 24 hours. The gases from the converter are cooled in silica S-pipes exposed to air, and then pass directly to the Glover tower.

The question of the amount of niter required for the successful working of a vitriol plant has been answered in various ways. It is usually given in percentages of sodium nitrate on the sulfur burnt, and figures ranging from 1.8% to 5% have been recorded. A careful examination of existing plants in England showed that 3% at the outside is all that is required for good working, provided the plant is intelligently operated, and there is ample Gay-Lussac capacity.

Different proposals for economy of niter have been made,¹ but the chief factors are those just mentioned.

Water Supply of Chambers. The water required in the chamber reaction:



is supplied (a) in the form of steam, blown into the chambers, or (b) in the form of a fine mist of droplets of liquid water produced by atomizing water by a special spraying apparatus. The first method was formerly the only one used, but it is being replaced by the use of water sprays.

If steam is used, it is taken from an ordinary low-pressure boiler, at 1 to $1\frac{1}{2}$ atm. Low pressure steam is more easily regulated than high-pressure, and the formation of droplets of water before it enters the chamber does no harm, provided these are driven on with the steam. The steam from a high pressure boiler may be passed through a reducing valve, or exhaust steam

1. O. Bender, U. S. P. 900688, 1908. F. Benker and H. Lasne, U. S. P. 250416, 1881; D. R. P. 17154; abst. Wag. Jahr. 1882, **28**, 257. F. Chappell, U. S. P. 375121, 1887. U. S. P. 378289, 1888. P. Derrig, U. S. P. 850820, 1907. S. Prazier, U. S. P. 388406, 1888. A. Johnson, U. S. P. 659236, 1900. H. Pauling, U. S. P. 898390, 1908. H. Petersen, U. S. P. 904147, 1908; 908696, 1909. J. Rigby, U. S. P. 292054, 1884. P. Salom, U. S. P. 755247, 1904. A. Tarand and P. Truchot, U. S. P. 1068021, 1913. M. Walsh, U. S. P. 292078, 1884. Hedenström, Chem. Ztg. 1914, **38**, 803.

from engines, e. g., the engine used for pumping the Gay-Lussac acid, may, of course, be used.¹ Production of steam by the heat of part of the burner gas has been proposed,² being conveyed to the chambers by cast iron pipes, with branches, protected by lagging, and with a slight back fall to the boiler so that condensed water may run back. The branch pipes are made from wrought iron, and need never be more than 1 in. diameter even for large chambers.

A single steam pipe of 1 in. diameter, introduced above, below, or even within, the pipe conveying gas, is sufficient for each chamber, of length not exceeding 130 ft., the pipe entering the upper part of the chamber. A better arrangement is to have two or more jets for each chamber.³ With a Glover tower, no jet is needed for the first chamber at the end, but one is placed 20 to 30 ft. along the side. A special arrangement for introducing steam has been described by Scheurer-Kestner.⁴ Passage of the gases through a hot-water tower has been proposed,⁵ and the mixing of the gases by a special spray producer has been described by A. Pohl.⁶

The amount of steam required depends on the quantity of sulfur burnt, and on the strengths of the chamber and Glover acids. On the assumption that all the chamber acid is 124° Tw., and that it is concentrated in the Glover tower to 148° Tw., each lb. of sulfur burnt requires:

$$\begin{array}{l} (1) \text{ for forming } 98 \text{ H}_2\text{SO}_4, 18 \text{ water} \dots\dots\dots = 0.5625 \text{ lb.} \\ \qquad \qquad \qquad \frac{32}{32} \qquad \qquad \qquad \frac{32}{32} \\ (2) \text{ for diluting to } 124^\circ \text{ Tw., i.e., } 70\% \text{ H}_2\text{SO}_4, 30 \times 98 \dots\dots\dots = 1.3125 \text{ lb.} \\ \qquad \qquad \qquad \frac{70 \times 32}{1.8750 \text{ lb.}} \end{array}$$

All this water is retained, since that escaping with the gas is absorbed by strong acid in the Gay-Lussac tower. A portion

1. H. Sprengel, E. P. 10798, 1886; abst. J. S. C. I. 1886, **5**, 668; Wag. Jahr. 1887, **33**, 505.

2. F. Kalbfleisch, E. P. 1618, 1877. A. Cellarius, D. R. P. 263941; abst. C. A. 1914, **8**, 219; Zts. ang. Chem. 1913, **26**, 605; Chem. Ztg. Rep. 1913, **37**, 546; Wag. Jahr. 1913, **59**, 1, 372. Societe L. Vogel, E. P. 17794, 1904. Belg. P. 180208, 181171, 1904; abst. J. S. C. I. 1905, **24**, 968; Chem. Ztg. 1906, **30**, 21; Mon. Sci. 1906, **65**, 178. H. Burbury, Belg. P. 232471, 1911. Schaefer & Budenberg, Dingl. Poly. 1875, **217**, 519.

3. Bräuning, Preuss. Zts. 1877, 137; Zts. Berg. Hütten-Salinenw. 1877, **25**, 132.

4. Wurtz, Dict. de Chim. **3**, 149.

5. Soc. Anon. Ing. L. Vogel, etc., E. P. 17794, 1904.

6. Zts. ang. Chem. 1912, **25**, 1220. Cf. A. Cellarius, Belg. P. 187896, 1905.

of the water introduced, however, comes from the evaporation in the Glover tower, and this must be deducted from the above amount:

Concentration from 124° (70%) to 148° (80%) "

$$\frac{10 \times 98}{70 \times 32} = 0.4375 \text{ lb.}$$

hence the water to be supplied = 1.8750 — 0.4375 = 1.4375 lb.

A certain excess must be added to allow for condensation in the pipes.

The second method of introducing the water is in the form of spray. H. Sprengel¹ first proposed to use water sprays, thus saving the cost of evaporation and reducing the chamber space, since steam increases the volume of the gases by its heat. In the Sprengel jet, steam under 30 lbs. pressure escapes through a platinum nozzle into the center of the water pipe. 20 lbs. of steam atomizes 80 lbs. of water. The Griesheim spray is produced without steam, by allowing water under 2 atm. pressure to impinge from a small platinum jet against a small platinum disc. Two rows of jets are introduced through tubes in the top of the chamber, being 20 ft. apart, the whole chamber being thus filled with fine mist. The water must be carefully filtered, to avoid stoppage of the jets.

Another type of jet has been devised by F. Benker,² in which the distance between the nozzle and the disc can be adjusted by a rod cut in a thread working in a nut, both being of platinum-iridium. A more recent form comprizes a platinum-iridium jet encased in antimonial lead, and without adjuster.

Körting Bros. jet,³ contains within the contracted part a metal spiral, held tightly in place by the pressure of the liquid, which imparts a whirling motion, so that it is projected uniformly in all directions as a spray. The nozzles are of platinum, or in a most recent type, of glass. The glass tube is drawn to a capillary point, where it is cut off quite straight so that the jet issues centrally. This should deliver 900–1000 liters per hour. The glass nozzle is fixed to the antimonial lead portion by means of

1. E. P. 3189, 1873. See Chem. News, 1875, **32**, 150. V. Defays, Belg. P. 201043, 1907.

2. F. Benker and E. Hartmann, Zts. ang. Chem. 1903, **16**, 861; abst. J. S. C. I. 1903, **22**, 1084.

3. Anon., Zts. ang. Chem. 1888, **1**, 404.

a thin rubber washer, the joint being made tight by the water pressure. The Körtling spiral of gun-metal is fixed inside by a thick rubber tube, the orifice of the tube being about 0.75 mm., that of the hard lead tube 4 mm. wide. With pressures of 3-5 atm. no drops are formed, but a fine mist.

All water used in sprays must be clarified, preferably by sponge-filters. An arrangement of sprays for chambers has been described by F. Benker.¹ Spray nozzles with discs of tantalum have been proposed.²

Many other types of spray producer have been described by H. Rabe,³ Poley,⁴ L. Santa,⁵ A. Düron,⁶ General Chemical Co.,⁷ J. Parent,⁸ D. H. Thomas,⁹ the Harkortsche Bergwerke und Chemische Fabriken,¹⁰ Scherfenberg & Prager,¹¹ A. Primavesi,¹² P. Jacobs,¹³ and others.

The use of water sprays in chambers has been discussed generally by O. Nagel,¹⁴ T. Norton,¹⁵ C. Gazel,¹⁶ G. Schüpphaus,¹⁷ O.

1. G. Lunge, "Sulfuric acid and Alkali," **1**, 734. P. Kestner, J. S. C. I. 1903, **22**, 333.
2. W. Szigeti, Chem. Ztg. 1918, **42**, 115; abst. J. S. C. I. 1918, **37**, 333-A. C. A. 1918, **12**, 2232.
3. Zts. ang. Chem. 1906, **19**, 2079. D. R. P. 237561, 246240; abst. C. A. 1912, **6**, 1508, 2503; Zts. ang. Chem. 1911, **24**, 1783; 1912, **25**, 1143; Chem. Zentr. 1911, **82**, II, 812; 1912, **83**, I, 1646; Chem. Ztg. Rep. 1911, **35**, 458; 1912, **36**, 286; Wag. Jahr. 1911, **57**, I, 418; 1912, **58**, I, 376; Zts. Schiess. Spreng. 1912, **7**, 98.
4. D. R. G. M. 3139.
5. E. P. 18615, 1913; abst. J. S. C. I. 1914, **33**, 485. D. R. P. 273665; abst. C. A. 1914, **8**, 2928; Zts. ang. Chem. 1914, **27**, 367; Chem. Zentr. 1914, **85**, I, 1862; Chem. Ztg. Rep. 1914, **38**, 310; Wag. Jahr. 1914, **60**, I, 295. F. P. 461641; abst. J. S. C. I. 1914, **33**, 199.
6. D. R. P. 221779.
7. U. S. P. 1032657; abst. C. A. 1912, **6**, 2676.
8. F. P. 462349, 1913.
9. E. P. 19867, 1912.
10. D. R. P. 275388; abst. J. S. C. I. 1914, **33**, 830; C. A. 1914, **8**, 3105; Zts. ang. Chem. 1914, **27**, 433; Chem. Zentr. 1914, **85**, II, 275; Chem. Ztg. Rep. 1914, **38**, 360; Wag. Jahr. 1914, **60**, I, 298.
11. D. R. P. 219789; abst. Zts. ang. Chem. 1910, **23**, 765; Chem. Zentr. 1910, **81**, I, 1073; Jahr. Chem. 1910, **63**, I, 523; Chem. Ztg. Rep. 1910, **34**, 159; Wag. Jahr. 1910, **56**, I, 407; Mon. Sci. 1913, **79**, 159; Chem. Zts. 1910, **9**, No. 1852; Zts. Schiess. Spreng. 1910, **5**, 114.
12. Chem. Ztg. 1906, **30**, 300; abst. Chem. Centr. 1906, **77**, I, 1804.
13. D. R. P. 141453; abst. Chem. Centr. 1903, **74**, I, 1323; Wag. Jahr. 1903, **49**, 268; Chem. Zts. 1904, **3**, 12.
14. J. S. C. I. 1914, **33**, 522; Chem. Ztg. 1914, **38**, 513; abst. C. A. 1914, **8**, 2509.
15. J. Ind. Eng. Chem. 1912, **4**, 534; abst. C. A. 1912, **6**, 2498.
16. Technique mod. May, 1911. Ind. Chim. 1911, **11**, 218; abst. C. A. 1911, **5**, 3612; Chem. Ztg. Rep. 1911, **35**, 464.
17. Metall u. Erz., 1915, 504; abst. Zts. ang. Chem. 1916, **29**, II, 171.

Guttmann,¹ to the original of which, the reader is referred.

Special arrangements of the chambers for use with water sprays have been disclosed by R. Delplace,² A. Gaillard,³ O. Guttmann,⁴ and L. Santa.⁵ F. Benker and E. Hartmann⁶ discuss the arrangement of draft for chambers with water sprays.

In general, one may say that taller chambers are more adapted to use with water sprays than steam. Thus, the Falding chamber (p. 1213) is especially suitable in this respect.

The regulation of the supply of steam or water spray to the chambers during operation is a matter of considerable importance. If too little water is added, chamber crystals are prone to form and choke the pipes, besides acting injuriously on the lead when decomposed by moisture. If too much water is supplied, the chamber acid becomes too diluted. Tests of the strength of the acid, therefore, afford a check on the water consumption. In British practice, the chamber acid is kept at a density of 120°–130° Tw., while on the Continent and in America a weaker acid, 106°–116° Tw., is usual. Lunge considers 106°–110° the best strength in the leading chamber.

The concentration of acid in the chambers beyond the leading chamber diminishes. Usually, in a series of three chambers, the strength in the second chamber is 10° less than that in the leading chamber. With more than three, the strength diminishes more gradually. In the last chamber it is kept below 75°, sometimes at 50°, if there is no Gay-Lussac tower. In all modern plants there is such a tower, and the acid in the last chamber may be of 90° Tw.

The injurious effects proceeding from deficient or excess steam are as follows: With too much, the acid becomes diluted,

1. J. S. C. I. 1903, **22**, 1333; abst. *Jahr. Chem.* 1903, **56**, 342.
2. F. P. 342117, 1904; abst. J. S. C. I. 1904, **23**, 900; *Chem. Zts.* 1904, **3**, 692. See also F. P. 333285, 1903; abst. *Chem. Zts.* 1904, **3**, 151, 291; *Mon. Sci.* 1904, **61**, 72.
3. F. P. 11732, 1908; abst. C. A. 1909, **3**, 1331; J. S. C. I. 1908, **27**, 1018. D. R. P. 203749, abst. *Wag. Jahr.* 1908, **54**, I, 371; *Chem. Zentr.* 1908, **79**, II, 1655; *Jahr. Chem.* 1905–1908, I, 1612; *Chem. Ztg. Rep.* 1908, **32**, 661; *Mon. Sci.* 1912, **77**, 49.
4. F. P. 18927, 1906; abst. J. S. C. I. 1907, **26**, 254; *Chem. Ztg. Rep.* 1908, **32**, 94; *Mon. Sci.* 1910, **73**, 33.
5. U. S. P. 1221913, 1917; abst. J. S. C. I. 1917, **36**, 548. F. P. 461641, 1913; abst. J. S. C. I. 1914, **33**, 199. Aust. P. 68855. E. P. 18615, 1913; abst. J. S. C. I. 1914, **33**, 485.
6. *Zts. ang. Chem.* 1906, **19**, 135. F. Benker, Belg. P. 176189, 1904.

and nitrogen oxides are converted into nitric acid, or even reduced to nitrogen or nitrous oxide. The nitric acid may be retained by the dilute acid in the chambers, and the supply of niter must be increased when the steam supply is cut down. If too little steam is supplied, the nitrosyl sulfuric acid formed cannot be completely decomposed, and may separate as chamber crystal. Also the acid may become so concentrated as to attack the lead. The real danger of corrosion, however, is when the water supply is increased and the chamber crystals are hydrolyzed with formation of nitric acid. The effects of an excess of steam (or water) are therefore more injurious than when too little is used.

The Supply of Air to the Vitriol Chambers. The oxygen required for the reaction in the chambers: $\text{SO}_2 + \text{H}_2\text{O} + \text{O} = \text{H}_2\text{SO}_4$ is always added in the form of air. Proposals to use pure oxygen¹ and ozone² have not been installed on account of the expense.

In calculating the composition of burner and chamber gases a knowledge of the densities of the gases which are contained therein is essential, the following table showing the most recent

Table of Densities of Gases

| Gas | Wt. of 1 lit. in Grams | Wt. of 1 cu. ft. in Lbs. | Vol. of 1 lb. in Cu. Ft. |
|---------------------|---------------------------|-----------------------------|-----------------------------|
| Air..... | 1.293 | 0.0807 | 12.39 |
| Oxygen..... | 1.429 | 0.0892 | 11.21 |
| Nitrogen..... | 1.251 | 0.0781 | 12.77 |
| Aqueous vapor..... | 0.7962 | 0.0497 | 20.12 |
| Sulfur dioxide..... | 2.927 | 0.1827 | 5.47 |

The normal composition of burner gas from brimstone is:

| | |
|---------------------|---------------------|
| Sulfur dioxide..... | 0.1123 cu. ft. |
| Oxygen..... | 0.0977 cu. ft. |
| Nitrogen..... | 0.7900 cu. ft. |
| | <hr/> 1.000 cu. ft. |

The weight of 1 cu. ft. of this gas at standard temperature and pressure (0° C. and 760 mm.) will therefore be.

$$0.1123 \times 0.1827 + 0.0977 \times 0.0892 + 0.7900 \times 0.0781 = 0.0909 \text{ lb.}$$

If the temperature of the gas in the burner exit is 100°, which is always much below the average temperature, the weight

1. T. Terrell, W. Hogg and J. Thomlinson, E. P. 3116, 1871.
2. P. Langlois and L. Thomassin, E. P. 3494, 1869.

of 1 cu. ft. of the gas will be $0.0909 \times \frac{273}{273 + 100} = 0.066$ lb.

But air at 35° is higher than the usual summer temperature, will weigh $0.0807 \times \frac{273}{273 + 35} = 0.071$ lb. Thus, the outside air is always heavier than the burner gas, and this causes the draught from the burners to the chambers. A second cause of the draught is the formation of sulfuric acid in the chamber, which diminishes the volume. A third cause is the chimney taking the nitrogen from the last chamber; this gas, when saturated with moisture and warm, being lighter than air.

The normal composition of pyrites burner gas is shown by the data for the oxygen required per 100 parts of sulfur:

375 parts of oxygen are required to oxidize the iron
 1000 parts of oxygen are required to form sulfur dioxide
 500 parts of oxygen are required to oxidize this to sulfur trioxide

Normal pyrites burner gases contain 8.95% SO_2 , 9.87% oxygen and 81.54% nitrogen. A calculation similar to that made for brimstone, shows that pyrites gas is even lighter, so that the draft will be somewhat better.

An excess of air supplied to the chambers is disadvantageous. It cools the gas and dilutes it, and hence diminishes the reaction, and wastes chamber space. The regulation of the air supply is made at the air-holes of the pyrites burners, by the fans, and by the chimney if one is used. The draft may also be maintained by a steam injector placed in the exit flue.¹ Steam injectors between the Glover tower and chambers, or between chambers, are impracticable because they introduce too much moisture into the system.

A suitable chimney placed after the Gay-Lussac tower is probably the best arrangement, although the regulation of the draft has then to be carefully watched.

The draft may be governed by a damper with a liquid seal, another arrangement being a pipe expanded into a drum containing a diaphragm perforated with holes so that the total cross section is somewhat greater than that of the pipe. These holes

1. A. Scheurer-Kestner, Bull. Soc. Chim. 1885, **44**, 98; abst. J. S. C. I. 1885, **4**, 494.

may be partially closed by clay until the required draft results. The draft may be automatically regulated.¹

The use of a fan blast is becoming more prevalent. The fans are of hard lead, enclosed in lead casings, and placed either between the Glover tower and the first chamber, or between the last chamber and the Gay-Lussac tower, or at both places, and are conveniently electromotor driven.² Stoneware fans, which can be used for temperatures not exceeding 70° are also used.³ Kestner fans of hard lead on an iron impeller⁴ are largely used for chamber plants. These make 300 700 r. p. m., require from 1½ to 1 h. p., and aspirate 1000 to 8000 cu. m. per hour. If two Glover towers are used, a fan is placed between them.⁵

Other arrangements for fan blast have been described by R. B. Wolf,⁶ the General Electric Co.,⁷ O. Mülhaiser,⁸ and others. Numerous ideas for accentuating the circulation of the gases in the chambers have been described.⁹ Some of these also

1. E. McFarland and the General Electric Co., U. S. P. 1112424; abst. C. A. 1914, **8**, 3841; Chem. Ztg. Rep. 1915, **39**, 119; Mon. Sci. 1915, **82**, 17. J. Cant, E. P. 15001, 1885. C. Vogt, E. P. 2690, 1875. W. Strype, E. P. 705, 1879.
2. F. Falding, Min. Ind. **7**, 672.
3. G. Petschow, Zts. ang. Chem. 1903, **16**, 12, 304. G. Plath, Zts. ang. Chem. 1903, **16**, 159; 1905, **18**, 1264; 1907, **20**, 444. F. Benker and E. Hartmann, Zts. ang. Chem. 1903, **16**, 861. See Chem. Ztg. 1902, **26**, 1057.
4. P. Kestner, Fifth Intl. Cong. Appl. Chem. 1905, **1**, 623; J. S. C. I. 1903, **22**, 333. See also Chem. Ztg. 1910, **34**, 734.
5. H. Nidenführ, D. R. P. 140825; abst. Zts. ang. Chem. 1903, **16**, 379; Chem. Centr. 1903, **74**, I, 1008; Jahr. Chem. 1903, **56**, 342; Chem. Ztg. 1903, **27**, 392; Wag. Jahr. 1903, **49**, I, 266; Chem. Zts. 1903, **2**, 713. F. Lüty, Zts. ang. Chem. 1905, **18**, 1253.
6. U. S. P. 1097784; abst. C. A. 1914, **8**, 2620.
7. E. P. 15293, 1913; abst. J. S. C. I. 1914, **33**, 482.
8. Zts. ang. Chem. 1902, **15**, 672; abst. J. S. C. I. 1902, **21**, 1026.
9. J. Hughes, U. S. P. 345140, 1886. 353222, 1886. N. Pratt, U. S. P. 546596, 1895; 652687, 652688, 652689, 652690, 1900. H. Hegeler and N. Heinz, U. S. P. 765834, 1904. T. Meyer, U. S. P. 688538, 688872, 1901. U. Wedge, U. S. P. 1104590, 1914. N. Heinz, U. S. P. 728914, 1903; 1057149, 1913. J. Thyss, U. S. P. 349241, 1886. W. Mills and C. Packard, U. S. P. 1112546, 1914. N. Pratt, U. S. P. 716142, 1902. St. J. Ravenel, U. S. P. 114042, 1871. C. Meigs, U. S. P. 1022493, 1912. O. Ehel, U. S. P. 860968, 1907. J. Hargreaves, U. S. P. 1303, 1839. G. Lunge, U. S. P. 485126, 1892. R. Evers, U. S. P. 767335, 1904. J. Graham, U. S. P. 736087, 1903. E. and J. Delplace, U. S. P. 446060, 1891. I. Lhime, U. S. P. 852390, 1907. R. Cellarius, U. S. P. 848631, 1907. A. Staub, U. S. P. 598351, 1898. H. Rabe, D. R. P. 246240, 237561, 1909, abst. J. S. C. I. 1912, **31**, 587. N. Heinz, D. R. P. 286972. G. Davis, E. P. 15459, 1912. D. Lowry, E. P. 2293, 1870. O. Nagel, Zts. ang. Chem. 1912, **25**, 1220; abst. J. S. C. I. 1912, **31**, 638.

describe arrangements for efficiently cooling the chambers.¹

The movement of gases in chambers, and the mode of action of fans, have been discussed by H. Porter,² H. Rabe,³ F. Lütty,⁴ Hüppner,⁵ M. Neumann,⁶ G. Schliebs,⁷ H. Nödenführ,⁸ E. Hartmann and F. Benker,⁹ T. Meyer,¹⁰ M. Feigensohn¹¹ and E. Raschig.¹²

Anemometers. The measurement of the draft in vitriol chambers is made by an anemometer. Some types, although suitable for other purposes, are not used in chamber work on account of the peculiar conditions.

Péclet's differential anemometer, as modified by Fletcher,¹³ is most used, and is based on the principle that a current of air passing the open end of a tube causes a lowering of pressure inside the tube. If, therefore, such a tube be introduced horizontally into a chimney, a partial vacuum will be induced inside the tube by the stream of gas passing up the chimney. This partial vacuum may be measured on an ordinary U-tube gauge filled with water or other liquid. The vacuum increases with the speed of the gas current; the pressure difference, however, is affected by the aspirating action of the chimney. This is obviated by introducing two tubes into the latter, one straight and the other bent at right angles so that the air blows into it. In the straight tube, the partial vacuum is increased by the aspirating action of the chimney, while in the bent tube it is correspond-

1. I. Lhime, U. S. P. 852390; abst. C. A. 1907, **1**, 2041; Chem. Ztg. Rep. 1907, **31**, 255. T. Oliver, U. S. P. 1229316; abst. C. A. 1917, **11**, 2265; J. S. C. I. 1917, **36**, 872; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 178.

2. J. S. C. I. 1909, **28**, 338; abst. C. A. 1909, **3**, 1062, 1671.

3. Zts. ang. Chem. 1905, **18**, 1735; abst. J. S. C. I. 1905, **24**, 1170.

4. Zts. ang. Chem. 1905, **18**, 1253; abst. J. S. C. I. 1905, **24**, 921.

5. Zts. ang. Chem. 1905, **18**, 2001; abst. Chem. Centr. 1906, **77**, I, 710.

6. Zts. ang. Chem. 1905, **18**, 1814; abst. Chem. Centr. 1906, **77**, I, 100, 1578. See also D. R. P. 169729, 1902; abst. Chem. Centr. 1906, **77**, I, 1637.

7. Zts. ang. Chem. 1905, **18**, 1900; abst. Jahr. Chem. 1905-1908, I, 1598.

8. Zts. ang. Chem. 1906, **19**, 61; abst. Jahr. Chem. 1905-1908, I, 1599.

9. Zts. ang. Chem. 1906, **19**, 132, 953; abst. Jahr. Chem. 1905-1908, I, 1600.

10. Zts. ang. Chem. 1906, **19**, 523; abst. Jahr. Chem. 1905-1908, I, 1595.

11. Chem. Ztg. 1906, **30**, 851; abst. Jahr. Chem. 1905-1908, I, 1592, 1594.

12. Zts. ang. Chem. 1905, **18**, 1281; abst. Jahr. Chem. 1905-1908, I, 1605. See also Ann. 1888, **248**, 123; abst. J. S. C. I. 1888, **7**, 747.

13. Third Alkali Inspector's Report, 1866, 51. See also Trans. Newcastle Chem. Soc. Jan. 26, 1871.

ingly decreased. One tube is connected with one limb of the U-shaped manometer, and the other with the other limb. The differences in level in this tube is thus a measure of the gas velocity.

Fletcher makes use of two cylinders 4 in. diameter, connected at the bottom by a narrow tube, the rise and fall of the liquid being observed by means of metal floats, on which a fine horizontal line has been marked by a lathe. The vernier permits the difference of level being read off to 0.001 inch. Ether, which is more mobile, and adheres less to glass than water, is used. The testing tubes are inserted into the flue by means of a cork and placed horizontally and so that the gas current blows into a bent tube. They are connected by rubber tubes to the manometer.

The velocities are obtained from the readings of the anemometer by means of tables.

The following precautions are necessary in using the instrument: (1) The anemometer must be located where it is not influenced by large differences of temperature, and may be placed any distance from the flue if air-tight connecting tubes are used. (2) The testing tubes should be introduced into the flue to the extent of one-sixth the diameter, the velocity in this position being assumed as a correct average. This point is disputed, and the measurement of the velocity in a flue of large section is a matter of difficulty.

Swan's anemometer consists of a U-tube containing ether, inclined at an angle of one in ten to increase the sensitiveness of the instrument, but the readings must then be divided by ten. The speeds are found from a table.¹

Other types of anemometers have been described by Kretz,² Ramsbottom,³ Scheurer-Kestner,⁴ F. Hurter,⁵ M. Bourdon,⁶ Fryer,⁷ Seger,⁸ C. Vogt,⁹ H. Rabe,¹⁰ P. Verbeek,¹¹ and others.

1. P. Hart, Chem. News, 1870, **21**, 200.

2. Dingl. Poly. 1868, **190**, 16; Bull. Soc. Ind. Mulhouse, 1868, **38**, 467.

3. Dingl. Poly. 1866, **180**, 334.

4. Dingl. Poly. 1875, **221**, 427.

5. Dingl. Poly. 1878, **229**, 160.

6. Compt. rend. 1882, **94**, 51; abst. J. S. C. I. 1882, **1**, 60.

7. Alkali Inspectors Rept. 1877-1878, 68.

8. D. R. P. 19426.

9. J. prakt. Chem. 1876, **122**, 284.

10. D. R. P. 111019; Zts. ang. Chem. 1900, **13**, 236; 1901, **14**, 950; 1903, **16**, 136.

11. Chem. Ztg. 1913, **37**, 1338, 1361; D. R. G. M. 560918, 559644.

Other methods of measuring speeds of gases are described by Kuhlmann¹ and J. B. Peregrin.² J. Partington and L. Parker (private communication) admit a measured amount of ammonia gas, measured at a constant rate by a Venturi meter, to the air stream, and analyze the latter by aspirating a measured volume through normal acid colored with litmus. This is useful for air currents, but cannot, of course, be used for acid gases, or gases which are to be used for reactions other than those involving the use of ammonia, such as oxidation (cf. Supply of Niter).

Seger's anemometer is now largely used, and consists of a calibrated U-tube surmounted by two cylindrical cups of equal width, the board on which it is fastened being provided with an adjustable sliding scale. The tube is filled with two non-miscible liquids, such as heavy paraffin oil and dilute colored alcohol, the junction being opposite the zero of the scale, before the measurement. The aspirating action is then exerted, which lowers the level. If the ratio of the sections of the tube is 20, the reading will be multiplied by 20. The scale is graduated directly to read in mm. of water.

Intensive Working and Reduction of Chamber Space. Reference has already been made to the increase of output attained in chambers by special arrangements, but particularly by increasing the amount of circulating nitrous compounds in the system. The two most important conditions for high production are efficient mixing of the gases and cooling.

K. Walter and E. Boeing³ describe the use of hollow acid-proof partitions built across the chambers, and arranged so that the gases enter the compartments through large holes near the bottom are discharged from holes near the top. The method is no longer used, as the walls are liable to collapse.

Gossage⁴ proposed to use chambers filled with coke, but impurities are then introduced into the acid, the walls of the chambers may be bulged out by the pressure of the coke, and the temperature rise is too high. Verstraet⁵ used stacks of bottom-

1. *Annee Indust.* 1878, 677; abst. *Chem. Ind.* 1878, **1**, 137.

2. *Ann. Chim. Analyt.* 1916, **21**, 223; abst. *J. S. C. I.* 1916, **35**, 1216.

3. *D. R. P.* 71908; abst. *Zts. ang. Chem.* 1894, **7**, 27; *Wag. Jahr.* 1894, **40**, 445; *Ber.* 1894, **27**, 175.

4. G. Lunge, "Sulfuric Acid and Alkali," **1**, 475.

5. *Bull. Soc. D'Encouragement*, 1865, 531; abst. *Jahr. Chem.* 1866, **19**, 845.

less stoneware jars in the chambers, supplying the nitrogen oxides by allowing the nitric acid to trickle over the jars.

N. Pratt¹ draws the gases by a fan through the first chamber, then through a tower packed with quartz, down which dilute sulfuric acid trickles, and then re-introduces them by a fan to the entrance to the first chamber. In a number of plants in the Southern States using this process, the chamber space is said to be reduced to 9 cu. ft. per lb. S per 24 hours.

T. Meyer's tangential chambers² have already been described. E. Hartmann³ places vertical air-cooled lead pipes in the chamber, the bottom of which is turned up around the lower ends of these pipes, thus forming hydraulic seals. F. Blau⁴ cools the gases in the first chamber by spraying in cold sulfuric acid, and obtains the optimum yield of acid from succeeding chambers by spraying in warm acid. F. Falding's process⁵ Lunge's plate tower, and the C. Opl system⁶ have also been treated. P. Gilchrist⁷ uses lead towers, 3 or 4 ft. diameter and 15 ft. high, with corrugated lead tubes open at both ends running across them horizontally like boiler tubes. The sides of the towers are enclosed in boarding so as to form a chimney, through which air circulates. Chamber gases enter together with steam or water spray, at the sides of the towers near the bottom, and pass upwards. Acid is condensed by impinging on the lead tubes, drips from one series of pipes to another, and eliminates nitrogen oxides. The gases leaving at the top are drawn into another series of pipe columns, and so on until reaction is complete. E. and J. Delplace⁸ use a lead chamber in the shape of a ring, with a segment cut out, and provided with two gas inlets at unequal heights, with distributing pipes leading from the upper to the lower part

1. U. S. P. 546596, 652687, 652688, 1900; abst. Mon. Sci. 1900, **56**, 210; J. Soc. Dyers Col. 1895, **11**, 222.

2. E. P. 18376, 1898; abst. J. S. C. I. 1899, **18**, 494. See also T. Meyer, Zts. ang. Chem. 1900, **13**, 742; 1911, **24**, 1520; abst. C. A. 1912, **6**, 795.

3. Chem. Ztg. 1897, **21**, 877; abst. J. S. C. I. 1897, **16**, 1015.

4. D. R. P. 95083; abst. Chem. Centr. 1898, **69**, I, 484; Chem. Ztg. 1897, **21**, 1083; Wag. Jahr. 1897, **43**, 424.

5. U. S. P. 932771, 1909; abst. Chem. Ztg. Rep. 1909, **33**, 542; Mon. Sci. 1910, **73**, 82.

6. U. S. P. 1012421, 1911; abst. C. A. 1912, **6**, 536; Mon. Sci. 1912, **77**, 130.

7. J. S. C. I. 1899, **18**, 459; abst. Chem. Centr. 1899, **70**, II, 232.

8. U. S. P. 446060; abst. J. A. C. S. 1891, **13**, 128.

of the chamber, which they consider a distinct improvement.

E. Thomson and W. Green¹ employ two towers, one for reaction and the other for absorption of nitrous gases. The burner gases are admitted at two points in the reaction tower, which is fed with nitric acid. The sulfuric acid condensed is drawn off and the nitrogen oxides absorbed from the residual gases by passing them through the second tower, which is fed with water. A Stinville² uses cool dilute sulfuric acid on the floor of the chamber to cool the gases, and furnish part of the water. W. Fulda³ treats the burner gases with nitric acid, which is regenerated by passing the gases through oxidizing towers. E. Barbier⁴ uses three reaction towers containing perforated pots, and one Gay-Lussac tower. The reaction towers are fed with nitric acid, the base of each tower consisting of a perforated plate under which is an acid pan heated by a separate fire. M. Neumann⁵ draws the burner gas through a plurality of Glover towers, and through alternate heating and cooling zones between the towers. A. Tait⁶ proposes to liquefy the SO₂ from the burner gas, so as to obtain the gas pure. This is then introduced with NO₂ under pressure into a chamber, into which air and steam are forced. The NO₂ is said to be oxidized to the (unknown) oxide NO₃, which mingles with the liquid SO₂, oxidizing the latter.

Methods of intensive working are discussed by J. Thede,⁷ A. Nemes,⁸ H. Petersen,⁹ and H. Rabe.¹⁰

Starting the Chamber Process. The first operation in starting a set of chambers is to cover the chamber bottoms with a layer of acid so as to provide a hydraulic seal. The acid should be at least 90° to 100° Tw., water or weaker acid being used only

1. U. S. P. 143202, 1873.
2. U. S. P. 765520, 1904; abst. Chem. Zts. 1904, **3**, 738; J. A. C. S. 1905, **27R**, 194.
3. U. S. P. 1048953, 1912; abst. C. A. 1913, **7**, 686; Mon. Sci. 1913, **79**, 99. Australian P. 17739, 1910.
4. U. S. P. 535882, 1895.
5. U. S. P. 729643, 1903. Belg. P. 163050, 1902; abst. J. A. C. S. 1904, **26R**, 29.
6. U. S. P. 86881, 1869.
7. Zts. ang. Chem. 1918, **31**, 2, 7; abst. J. S. C. I. 1918, **37**, 464-A; C. A. 1918, **12**, 2663. D. R. P. 312024, 1918; abst. J. S. C. I. 1919, **38**, 680-A.
8. Zts. ang. Chem. 1911, **24**, 387; Chimiste, 1911, **2**, 161; abst. C. A. 1911, **5**, 2418; J. S. C. I. 1911, **30**, 417.
9. Zts. ang. Chem. 1911, **24**, 877, 1811; abst. J. S. C. I. 1911, **30**, 743; C. A. 1911, **5**, 3129, 3882.
10. Zts. ang. Chem. 1910, **23**, 8; abst. C. A. 1910, **4**, 1225.

in extreme cases, and if acid is not available, it should be transported if possible. If weak acid or water is used, the nitrogen oxides dissolve in it as nitric acid, which then attacks the lead.

The burners are next charged with ore and lighted, and the burner gas, together with nitrogen oxides obtained from niter pots or otherwise, introduced into the chambers. A large stock of niter is put in at the beginning, so as to provide the circulating niter. About 12 to 15 parts of niter to 100 sulfur burnt may be used at the commencement of the process, being cut down to about 3 parts when the chambers are in normal working operation.

When the drip tests show sulfuric acid is being formed in the chambers, steam or water spray is introduced, usually during the second day. The plant should be in operation about four days after starting.

If the chambers have to be discontinued for repairs, the reverse process is carried through. The burners are stopped by closing all the air holes and ceasing to charge with ore. Then the niter supply is cut off, but the steam is kept on as long as the gas in the last chamber shows any outward pressure. When the steam is shut off, the outlet damper is closed, and air allowed to enter at some point to prevent the chamber walls collapsing by the outer pressure. The steam should be discontinued when the drips test 100° Tw. Acid continues to be produced, but when the drips cease to operate, the process has finished and all openings are closed.

Vitriol Chamber Temperatures. The successful operation of a set of vitriol chambers implies that a definite set of temperatures shall be maintained in the various portions of the apparatus, and the observation and control of these temperatures is a matter of great importance. The thermometers inserted in the chambers have already been described in connection with chamber fittings.

Considerable diversity of opinion exists as to the optimum temperatures for working, and this will also depend as to whether intensive working is adopted or not. In normal working, the first chamber may be at 50°-65°, i. e., too hot to be touched with the hand for any length of time. The second chamber may be at 40°-60°, and the inside temperature of the last chamber may

be 30°–40° or less,¹ about 35° being considered optimum.

The temperatures of the chambers are influenced by the heat in the burner gases, that of the steam introduced, in some cases by the heat of the sun if the chambers are unprotected, by radiation, and by wind. The chief factor, however, is the heat of the reactions taking place in the chambers.

When a stationary state has set in, a variation of temperature of more than 5° may be taken as indicative of some irregularity in working. Owing to the heat of reaction, the temperature in the first chamber will be higher than that of the gases leaving the Glover tower.

An abnormal state is sometimes met with in which the temperature of the first chamber sinks while that of the last chamber rises. This is caused by lack of water, or excess of steam or air. In remedying the defect, an additional supply of niter must be used to restore the first chamber to the normal state.

Proposals for cooling the chambers, or the gases between the Glover tower and the chambers, have been made.²

Irregularities in Chamber Work. When the chambers are working irregularly, losses of sulfur dioxide and also of nitrogen oxides result, one main cause being a deficiency of the latter in the chambers. This does not, of course, mean that a large consumption of niter is required, since the bulk of the nitrous gases are in circulation in the system, but that an adequate supply must be introduced into the chambers at the start, and maintained by continuous addition to make good any small losses of nitrous gases. The use of ammonia oxidation apparatus, which permits of a more exact regulation of the supply of nitrogen oxides than any other method, is especially valuable in this respect.

The effects of a deficiency of niter are various. The rate of formation of sulfuric acid is too slow, and much sulfur dioxide passes out unoxidized. In the back chambers this sulfur dioxide

1. G. Lunge and P. Naef, *Chem. Ind.* 1884, **7**, 17. W. Crowder, *J. S. C. I.* 1891, **10**, 301. G. Eschellmann, *J. S. C. I.* 1884, **3**, 135.

2. N. Pratt, *U. S. P.* 715142, 1902; *abst. Chem. Zts.* 1903, **2**, 375, 528; *J. A. C. S.* 1903, **25R**, 337; *Mon. Sci.* 1903, **59**, 99. A. Stinville, *D. R. P.* 144084; *abst. Zts. ang. Chem.* 1903, **16**, 949; *Chem. Centr.* 1903, **74**, II, 776; *Chem. Ztg.* 1903, **27**, 900; *Wag. Jahr.* 1903, **49**, I, 267; *Mon. Sci.* 1904, **61**, 81; *Chem. Zts.* 1904, **3**, 164, 276, 291. F. P. 350363; *abst. Chem. Zts.* 1906, **5**, 37; *Mon. Sci.* 1907, **67**, 598. A. Zanner, *Zts. ang. Chem.* 1907, **20**, 6; *abst. C. A.* 1907, **1**, 768. L. Fromont, *E. P.* 4861, 1907; *abst. J. S. C. I.* 1907, **26**, 1198. B. Hart and H. Bailey, *J. S. C. I.* 1903, **22**, 473.

will bring about denitration of nitrous vitriol in the wrong place. Much NO is formed, and the color of the chambers is pale. Owing to the relative excess of water, the nitrous vitriol formation is retarded, and the NO, in presence of water and oxygen, forms nitric acid, which dissolves in the acid at the bottom of the chamber, causing still further deficiency of niter. Such acid may attach the chamber lead. Any NO passing to the Gay-Lussac tower is not absorbed. Under certain conditions it is said that nitrous oxide may be formed in the chamber reactions with faulty working, leading to further loss of niter. In remedying lack of niter, it is always necessary to introduce many times more niter than the amount wanting.¹

Loss of niter is brought about by incomplete absorption in a Gay-Lussac tower, of inadequate size, and by leakage. Loss by reduction to oxides below NO, or to nitrogen, is probably very rare, if ever. Loss by reduction of nitrous vitriol by the coke packing of the Gay-Lussac tower, whereby NO is produced, is said to take place.² An important research on niter losses was carried out by J. Inglis,³ in which he condensed the chamber gases by cooling in liquid air, and found that the liquid could be separated by fractionation into the following constituents: N₂, NO, N₂O, CO₂, SO₂, NO₂ and H₂SO₄. The quantity of N₂O found was extremely small, about 0.002%, so that "chemical losses" may be practically dismissed. The greater part of the loss is due to incomplete absorption in the Gay-Lussac tower. The volume of the latter may be as much as 2%-3% of the chamber space; further increase is said to have very little effect.⁴ Regular chamber working is only attainable by proper control.⁵

Gas Distribution and Speed of Acid Formation. The manner in which the gases pass through the vitriol chambers, and the

1. G. Eschellmann, J. S. C. I. 1884, **3**, 136; abst. Jahr. Chem. 1884, **37**, 1727.

2. G. Lunge and P. Naef, Chem. Ind. 1884, **7**, 11. F. Benker and E. Sorel, Zts. ang. Chem. 1889, **2**, 279. See also F. Hurter, Chem. News, 1879, **39**, 170, 237. G. Lunge, Chem. News, 1879, **39**, 193, 237. G. Davis, Chem. News, 1879, **39**, 205, 215. E. Jackson, Chem. News, 1879, **39**, 227. J. Mactear, Chem. News, 1879, **39**, 232. J. Cox, Chem. News, 1879, **39**, 249. S. Hamburger, J. S. C. I. 1889, **8**, 167.

3. J. S. C. I. 1904, **23**, 643; 1906, **25**, 149; 1907, **26**, 670.

4. G. Bailey, J. S. C. I. 1887, **6**, 92; abst. Jahr. Chem. 1887, **40**, 8.

5. H. Cory, Chem. Trade J. 1917, **60**, 297; abst. C. A. 1917, **11**, 1887. See also H. Pemberton, Dingl. Poly. 1883, **248**, 424; abst. J. S. C. I. 1883, **2**, 414.

velocity with which acid is produced in various parts of the chambers, are questions of practical importance in chamber design. Many experiments have been made on these matters,¹ but the results are not free from inconsistencies. The method of placing lead dishes in various parts of the chambers and comparing the amounts of acid collecting in them is unreliable, as Lunge points out, since the dishes may act as condensing surfaces for acid, as well as serving as receptacles for the shower of acid formed in the chamber.² In this connection the experiments of P. Naef³ are of interest. This observer placed inside the chamber on one side a lead tray with a cover which could be suspended above it at various distances. He found the amount of acid collected was very much the same wherever the cover was placed, which seems to dispose of the theory that the dish collects the acid shower, even if the latter falls in a slanting direction. It appears that the acid collecting in the tray is formed from the fine mists which float about in all directions, and condenses on solid surfaces on which it impinges.

Tests on the vitriol chamber gases have been made by J. Mactear,⁴ W. Crowder,⁵ and particularly by G. Lunge and P. Naef,⁶ and S. Retter.⁷ Lunge and Naef found that in normally working chambers no "free" nitrogen dioxide is ever present, but there is always an equivalent amount of nitric oxide, so that the mixture behaves on absorption as nitrous anhydride, N_2O_3 . In the first chamber, where the reaction was most vigorous, an excess of NO was found, but in later chambers NO and NO_2 were found in equivalent amounts. When the supply of niter is abnormally high, free NO_2 may appear, so that this gas may occur in chambers working on the intensive system, as Lunge points out. The presence of an excess of oxygen (air) in the chambers on the other hand, has no influence on the proportion of NO and NO_2 .

The distribution of gases in the chambers was found to be

1. G. Lunge, "Sulfuric acid and Alkali," 4th ed. 955.
2. J. Mactear, J. S. C. I. 1884, **3**, 224. H. Smith, "On the Chemistry of Sulfuric Acid Manufacture," 1873.
3. Chem. Ind. 1885, **8**, 287; abst. Jahr. Chem. 1885, **38**, 2060.
4. J. Mactear, J. S. C. I. 1884, **3**, 224. H. Smith, "On the Chemistry of Sulfuric Acid Manufacture," 1873.
5. J. S. C. I. 1891, **10**, 295; abst. Jahr. Chem. 1891, **44**, 2627.
6. Chem. Ind. 1884, **7**, 5; abst. J. S. C. I. 1884, **3**, 258, 633.
7. Zts. ang. Chem. 1891, **4**, 4; abst. J. S. C. I. 1891, **10**, 364.

as follows: The percentage of SO_2 diminishes very rapidly, in the middle of the first chamber being only about 2%, as compared with 7% in the entering gas, so that about 70% of the acid is produced in the first portion of the first chamber. In the second half of the first chamber only about 4% SO_2 is oxidized. On entering the second chamber, the reaction revives, probably owing to the cooling and mixing of the gases in the pipes connecting the chambers. In the center of the second chamber only 0.2% to 0.4% of the SO_2 is left, showing an absorption of 20% of the initial SO_2 in that chamber. From this point, the oxidation of the SO_2 proceeds very slowly, and a little always passes unchanged into the Gay-Lussac tower. The diminution of the reaction in the last part of the first chamber has been confirmed by other experiments made by F. Hurter,¹ P. Naef,² A. Schertel,³ E. Sorel,⁴ and S. Retter.⁵

The distribution of the gases in the chamber was also studied by G. Lunge and P. Naef. For this purpose gas was aspirated from three different positions in the chamber, lying in the same vertical line near the side of the first chamber, and only slight differences in composition were found. When the tubes were passed through the chamber top at the center line, reaching down to different depths, only minor variations were noted. It was found, however, that much less SO_2 was present in the first experiments, near the chamber walls, than when the gas was taken from the middle of the chamber. Thus the reaction is a little more energetic near the walls than in the center of the chamber. These experiments show that the gases in the chambers are quickly intermingled, but there are noticeable variations between the center of the chamber and the walls.

The results of Lunge and Naef are in agreement with a theory propounded by K. Abraham,⁶ on the course taken by the gases in the chambers. According to this investigator, the burner gases on entering the first chamber meet a gas whose temperature and composition differs but slightly from its own. The entering

1. J. S. C. I. 1882, **1**, 8, 49, 83. Reprinted in Wag. Jahr. 1882, **28**, 240.
2. Chem. Ind. 1885, **8**, 285; abst. Wag. Jahr. 1885, **31**, 213.
3. Chem. Ind. 1889, **12**, 80. J. S. C. I. 1889, **8**, 283. Sächs. Jahr. Berg. u. Hüttenw. 1890, 138.
4. Zts. ang. Chem. 1889, **2**, 270; abst. J. S. C. I. 1890, **9**, 175.
5. Zts. ang. Chem. 1891, **4**, 4; J. S. C. I. 1891, **10**, 364.
6. Dingl. Poly. 1882, **245**, 416; abst. J. S. C. I. 1882, **1**, 406.

gas therefore spreads over the front part of the chamber from top to bottom, and is slowly propelled by the draft along the chamber over its transverse section. The formation of sulfuric acid also takes place regularly and equally at all points of a transverse section taken at right angles to the chamber. According to Lunge and Naef's work, the latter assertion is incorrect. The heat of reaction raises the temperature of the interior, while that at the side walls is kept down by radiation. A difference of temperature and density is, therefore, produced in the gases which leads to their rising in the center of the longitudinal section, and descending along the sides of the chamber. This motion goes on continually, and is modified only at the ends of the chamber. Thus, the gases travel in vertical layers at right angles to the length of the chamber from the front to the back end, but each small portion of gas describes a spiral line, the axis of which is parallel to the length of the chamber.

The motion of the gases in the chambers has also been studied by H. Porter,¹ who experimented with a glass model of a chamber. He concludes that the gases should be admitted to the chamber at the bottom, and steam at either end so as to mix the gases. E. Hartmann and F. Benker,² T. Meyer,³ and H. Rabe,⁴ propose to introduce the gases in the middle of the front wall in an upward direction, so as to proceed in spiral lines; K. Beskow⁵ and O. Niedenführ⁶ are not in agreement with Abraham's theory.

The time during which the gases remain in the chambers has been calculated by Schwartzenberg at $5\frac{3}{4}$ hours, by Bode at

1. J. S. C. I. 1903, **22**, 476; abst. Tech. Chem. Jahr. 1903, **26**, 67; Chem. Zts. 1903-1904, **3**, 17.
2. Zts. ang. Chem. 1903, **16**, 861; abst. J. S. C. I. 1903, **22**, 1084.
3. Zts. ang. Chem. 1903, **16**, 555, 927; abst. Chem. Ztg. 1903, **27**, 858; Tech. Chem. Jahr. 1903, **26**, 68.
4. Zts. ang. Chem. 1910, **23**, 8. D. R. P. 237561; abst. C. A. 1912, **6**, 1508; Zts. ang. Chem. 1911, **24**, 1783; Chem. Zentr. 1911, **82**, II, 812; Chem. Ztg. Rep. 1911, **35**, 458; Wag. Jahr. 1911, **57**, I, 418; Zts. Schiess Spreng. 1912, **7**, 98.
5. Zts. ang. Chem. 1911, **24**, 200; abst. J. S. C. I. 1911, **30**, 281.
6. D. R. P. 189238; abst. C. A. 1908, **2**, 1074; Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 1949; Jahr. Chem. 1905-1908, I, 1251; Chem. Ztg. Rep. 1907, **31**, 549. D. R. P. 189330; abst. C. A. 1908, **2**, 1075; Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 1951; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1907, **31**, 549; Wag. Jahr. 1907, **53**, I, 332. D. R. P. 189834; abst. Zts. ang. Chem. 1908, **21**, 794; Chem. Zentr. 1907, **78**, II, 1953; Jahr. Chem. 1905-1908, I, 1611; Chem. Ztg. Rep. 1907, **31**, 549; Wag. Jahr. 1907, **53**, I, 332; Chem. Zts. 1907, **6**, No. 362.

3³/₄ hours, and by Lunge (with 20 cu. ft. per lb. S per 24 hours, which is very large; 8% SO₂ in the burner gases, and 4% niter), at 2³/₄ hours. In modern plants the time must be less than 1 hour. Sorel, calculating for intensive working, with 11.2 cu. ft. per lb. S finds 1 hour 34 mins. One reaction at least in the process, viz., the oxidation of NO to NO₂, will require an appreciable time for completion. Another factor is the time required for the acid mist to deposit.

Proposals for condensing the acid mist electrically have been made by A. Johnson,¹ and by W. Whitney.² R. Winsloe and B. Hart³ cool and mix the gases between the different chambers by passing them through mains containing air cooled batteries of tubes. F. Falding⁴ passes the gases from the Glover tower through a second tower directly supplied with hot gases from the pyrites burners, the acid being concentrated in this manner. F. Curtius & Co.⁵ allow the burner gases to enter at a maximum temperature of 150°; the first tower of the system being sprayed with a relatively small amount of nitric acid or nitrous vitriol. J. Harris and D. Thomas⁶ admit the gases to the chamber at the bottom, direct them round the walls, where they issue from the center of the top. A hollow central column is provided, standing in the pan and having an open top for the exit of the gases. Sprays direct liquid on a curtain and the outside of the column. The General Electric Co.⁷ arrange the blower causing movement of gases through the chambers to act by induction on the gases of the last chamber, so that the destructive action of the gases on the blower is avoided, the gases being drawn through the chambers. T. Murray and E. Ricketts⁸ pass the outlet fumes of the plant through a thin layer of sodium carbonate solution, then with the entrained liquid through parallel screens, to remove acid fumes. A graphic method of recording the working of a chamber system

1. E. P. 17928, 1900; abst. J. S. C. I. 1901, **20**, 250.
2. U. S. P. 1022012; abst. C. A. 1912, **6**, 1573; Mon. Sci. 1912, **77**, 132.
3. E. P. 20142, 1901; abst. J. S. C. I. 1902, **21**, 1183.
4. E. P. 17602, 1893; abst. Mon. Sci. 1894, **44**, 918.
5. Holl. P. 1172, 1913; abst. C. A. 1916, **10**, 1581.
6. E. P. 104461, 1916; abst. C. A. 1917, **11**, 1889; J. S. C. I. 1917, **36**, 502; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 178. See also H. Royal-Dawson, E. P. 135359, 1919; abst. J. S. C. I. 1920, **39**, 62-A.
7. E. P. 15293, 1913; abst. C. A. 1915, **9**, 132; J. S. C. I. 1914, **33**, 482.
8. U. S. P. 1132679, 1915; abst. J. S. C. I. 1915, **34**, 491.

has recently been described and illustrated by W. Coleman.¹

Analysis of the Chamber Exit Gases. The exit gases from a chamber plant are required by law to contain less than a stated amount of acid vapors, either existing as gaseous SO_2 or nitrogen oxides, or as a mist of H_2SO_4 . The total acidity, expressed in terms of grains SO_3 per cu. ft. is usually returned.

The acidity is determined by aspirating a measured volume of the exit gas through an absorption vessel containing a measured volume of standard alkali, and titrating the amount neutralized. Special forms of apparatus have been described by J. Mactear,² G. Davis,³ W. Younger,⁴ W. Strype,⁵ R. Carpenter and E. Linder,⁶ H. Watson,⁷ W. Coleman,⁸ W. Lovett,⁹ G. Knorre and K. Arndt,¹⁰ and G. Lunge.¹¹

Various forms of absorption vessels have been used. Ordinary gas washing bottles may be used, especially if the inlet tube is closed at the bottom and perforated. Mitscherlich's tubes or Todd's modification may be used. The aspirator is usually a large tubulated bottle with a tap below for running off water into a graduated cylinder, and a stopcock above for connecting with the absorption apparatus.

The *total acidity* is determined with alkali and litmus as indicator, and is returned in grains SO_3 per cu. ft., or in any other unit desired. Methyl orange should not be used, as it is destroyed by the nitrogen oxides in the gas. Alizarin-red, however, gives good results.

A continuous test, extending over 24 hours, may be made, the volume of gas reduced to S. T. P. being recorded by a calibrated gasometer placed after the absorption vessel, a filter pump with a regulating arrangement being used as aspirator. The rate of aspiration should be about 1 cu. ft. per hour. Tables for the

1. J. S. C. I. 1906, **25**, 1201; abst. C. A. 1907, **1**, 768.
2. Chem. News, 1877, **36**, 49; abst. Jahr. Chem. 1877, **30**, 1138, 1145.
3. Chem. News, 1880, **41**, 188; abst. Jahr. Chem. 1880, **33**, 1286.
4. J. S. C. I. 1887, **6**, 347; abst. Jahr. Chem. 1887, **40**, 2490.
5. Trans. Newcastle Chem. Soc. 1880, **4**, 357; abst. Chem. News, 1879, **39**, 288.
6. J. S. C. I. 1902, **21**, 1490; abst. Chem. Centr. 1903, **74**, I, 481.
7. J. S. C. I. 1903, **22**, 1279; abst. Jahr. Chem. 1903, **56**, 344.
8. J. S. C. I. 1906, **25**, 1201; abst. Jahr. Chem. 1905-1908, I, 1597.
9. J. S. C. I. 1882, **1**, 210; abst. Wag. Jahr. 1882, **28**, 274.
10. Ber. 1899, **32**, 2136; abst. J. S. C. I. 1899, **18**, 1156.
11. "Sulphuric Acid and Alkali," **1**, 974.

reduction of gaseous volumes have been given,¹ or a chart may be constructed. The absorption apparatus consists of four bottles or tubes, each of the first three containing 100 cc. *N* NaOH solution, and the fourth distilled water. The contents of the bottles are mixed, and divided into three equal parts, one being retained in case of an accident. The first bottle is titrated with *N*/ H_2SO_4 for total acidity. Let x cc. of acid be required. The second portion of liquid is poured into a warm solution of KMnO_4 strongly acidified with sulfuric acid. A small excess of permanganate must be present, which is then reduced by adding a few drops of sulfurous acid until only a faint pink color remains. All nitrogen acids are now present as HNO_3 . 25 cc. of a solution containing 100 gm. crystallized ferrous sulfate per liter are added to a flask with 20-25 cc. pure concentrated H_2SO_4 , and the mixture allowed to cool. The solution to be tested is now added, and the air displaced by a stream of CO_2 . The liquid is then boiled for 15 mins. to 1 hour, according to the amount of HNO_3 present, until the dark color changes to a clear yellow. The unoxidized FeSO_4 is then titrated with $N/2$ KMnO_4 (1 cc. = 0.004 gm. O), of which y cc. are required. Let 25 cc. FeSO_4 solution require z cc. $N/2$ KMnO_4 .

If V cu. ft. of gas, at S. T. P., were aspirated, the required amounts of substances are given by the equations:

- | | |
|---|--|
| 1. <i>Total Acidity</i> in grains per cu. ft. | 3. <i>Sulfur</i> in grains per cu. ft. |
| $\text{SO}_3 = 1.85(100 - x)/V$ | $\text{S} = 0.12346(600 - 6x - z + y)/V$ |
| 2. <i>Nitrogen</i> in grains per cu. ft. | |
| $\text{N} = 0.10803(z - y)/V$ | |

If nitrogen acids are not required separately, 100 cc. *N*/NaOH may be taken in a bulb-tube, and the excess titrated with standard acid and phenolphthalein. If x cc. of acid are required:

$$\text{Total acid as grains } \text{SO}_3 \text{ per cu. ft.} = 0.617(100 - x)/V$$

Hydrogen peroxide may be added to the soda, but as it is usually acid, a correction must be applied. A solution of sodium peroxide, prepared by adding small amounts of Na_2O_2 to a mixture of ice and water, and diluting to normal, may also be used, if nitrogen oxides are present.

If acid mist is present, it passes through the bottles, and a special absorption vessel must be used. The gas enters, and is

1. "Technical Chemists' Handbook."

broken up by rubber rings contained in the tube, which are clipped from tubing. The upper bulb is $\frac{3}{4}$ in. wide, the lower one $\frac{5}{8}$ in., and the bottom opening $\frac{1}{4}$ in. The exit tube is filled with glass wool, and is washed down after the experiment.

Since NO may escape in the above apparatus, it is advisable to add a bulb tube containing acidified KMnO_4 , which is not absorbed by soda and H_2O_2 . Oxygen in the exit gas may also be determined.

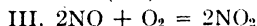
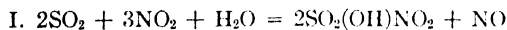
Theory of the Lead-Chamber Process. The reaction of importance in the chamber process is the conversion of sulfur dioxide into sulfuric acid. This does not take place to an appreciable extent in presence of atmospheric oxygen alone, nor does the oxygen introduced in the form of niter nearly account for the change. It is evident, therefore, that the reaction involves some catalytic reaction brought about by the nitrogen oxides introduced into the chambers, the exact nature of which reaction is still in dispute.

Clément and Désormes,¹ who observed the essential features put forward a theory of the part played by the nitrogen oxides which, with some unimportant modifications, is essentially that accepted today. They assumed the nitrogen oxides gave up oxygen to the sulfur dioxide, converting it into sulfuric acid, and were reduced to a lower oxide, NO, which is capable of taking up oxygen directly from the air present, being thereby reconverted into higher nitrogen oxides which again enter into the cycle of reactions. The nitrogen oxides therefore, act as a carrier of oxygen, taking it from the air and transferring it to the sulfur dioxide. Clément and Désormes also noticed that where only a small amount of moisture was admitted, white star-shaped crystals are formed, which in contact with water decompose with effervescence, producing oxides of nitrogen in the form of brown fumes, and leaving dilute sulfuric acid. These crystals were afterwards shown to be nitrosulfonic acid HSNO_3 , which Clément and Désormes suspected probably plays some part in the cycle of changes which involves the alternate reduction and oxidation of the nitrogen oxides.

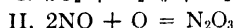
H. Davy in 1812 showed that the presence of water is essen-

1. Ann. Chim. Phys. 1806, **53**, 329; J. des Mines, 1806, **20**, 227; Nicholson's J. 1807, **17**, 41; Gehlen J. 1807, **4**, 457; Gilb. Ann. Phys. 1818, **58**, 67.

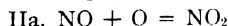
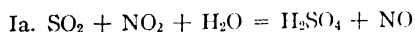
tial. In the dry state the gases do not interact, but if a little water is added the chamber-crystals, or nitrosulfonic acid, are produced; he regarded these as the intermediate compound in the cycle of reactions:



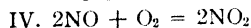
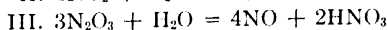
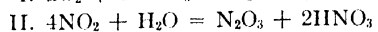
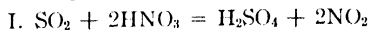
J. Berzelius¹ considered the chamber-crystals were not normally produced as an intermediate product, but that oxygen is directly carried over from nitrogen oxides to sulfur dioxide, producing nitric oxide, which is then reoxidized:



At that time no distinction was made between N_2O_3 and N_2O_4 , and both were called "nitrous acid," the name used by Berzelius for the intermediate higher nitrogen oxide. Later writers therefore often wrote Berzelius' theory in the form:



In 1844 an entirely different theory was propounded by E. Peligot,² in which the catalytic substance was supposed to be nitric acid. This theory had a following in France for a considerable time, but rested primarily on experimental errors. The following equations represent Peligot's theory:



Although it is true, as Peligot stated, that sulfur dioxide is oxidized by *concentrated* nitric acid with formation of sulfuric acid and nitrogen dioxide, yet as was pointed out by R. Weber,³ nitric

1. Lehrbuch, 1835, **2**, 12.
2. Ann. Chim. Phys. 1844, (3), **12**, 263; Compt. rend. 1844, **19**, 420; J. prakt. Chem. 1845, **34**, 117; Ann. 1844, **52**, 221.
3. Pogg. Ann. 1866, **127**, 543; 1867, **130**, 329; abst. Jahr. Chem. 1866, **19**, 125; 1867, **20**, 176; Berl. Acad. Ber. 1866, 57; J. prakt. Chem. 1866, **97**, 487; 1867, **100**, 37; Zts. Chem. 1866, **9**, 329; Chem. Centr. 1866, **37**, 362; 1867, **38**, 325; Dingl. Poly. 1866, **181**, 297; 1867, **184**, 246; Bull. Soc. Chim. 1867, **7**, 151; **8**, 26; Instit. 1866, 415; Wag. Jahr. 1866, **12**, 144; 1867, **13**, 166; Poly. Centr. 1866, **32**, 860; 1867, **33**, 576; Poly. Notizbl. 1866, **21**, 212; Deut. Ind. Ztg. 1866, 284; Chem. News, 1867, **16**, 12.

acid of the concentration in which it can exist in the chamber has practically no action on sulfur dioxide in the cold, and acts only slowly when heated to 80°. Peligot's theory has been abandoned since the appearance of Weber's work.

Weber showed that sulfur dioxide was rapidly oxidized by water which has absorbed nitrous fumes and therefore contains nitrous acid, and he considered that nitrous acid was the principal agent in the process. Nitric acid in solution was acted on only very slowly, and Weber made the interesting observation that nitric acid dissolved in sulfuric acid is more easily reduced by sulfur dioxide in moderately dilute solutions than in concentrated sulfuric acid. Weber's theory of the chamber process in outline, is as follows: Sulfur dioxide is oxidized mainly by the nitrous acid, which passes into nitric oxide, but this process goes on only in aqueous solution, such as is formed by dissolving nitrogen dioxide in water (in which case some nitric acid is formed and remains unchanged), or by dissolving nitrogen trioxide in water (in which case nitrous acid only is formed, which is active).

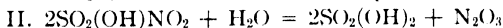
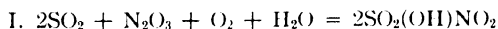
About the same time as the enunciation of Weber's theory, C. Winckler advanced an analogous theory, but he assumed that nitrogen dioxide was the active agent, whereas Weber contended this to be the trioxide or the anhydride of nitrous acid. The most important point of difference, however, was that Weber followed Berzelius in considering that chamber-crystals did not play any part as an intermediate product, whereas Winckler reverted to Davy's theory, in which they play the role of an intermediate product.

In 1884 the theory received some important additions as the result of experimental work carried out in actual chambers at the "Uetikon" Works, Zurich, by G. Lunge and P. Naef.¹ In the first place it was found that nitric oxide in the dry state and out of contact with sulfuric acid, combines with oxygen to form nitrogen dioxide. In the presence of moisture and excess of oxygen only nitric acid is ultimately formed. Dilute sulfuric acid (sp. gr. 1.405) acts like water, but a small amount of nitrous acid is formed. But if *concentrated* sulfuric acid is brought in presence of an excess of oxygen and nitric oxide passed into it, that part

1. Chem. Ind. 1884, **7**, 5; J. C. S. 1885, **47**, 465; Ber. 1885, **18**, 1384; 1888, **21**, 3323; abst. J. S. C. I. 1884, **3**, 258, 633; Jahr. Chem. 1884, **37**, 1725; 1885, **38**, 2061.

of the NO in immediate contact with the acid is oxidized only to the stage of N_2O_3 , and is absorbed as nitrosulfonic acid: $2NO + O + H_2SO_4 = 2HSNO_5 + H_2O$, whereas the NO out of contact with the acid is oxidized to NO_2 , which dissolves to form a mixture of equal amounts of nitrosulfonic and nitric acids: $2NO_2 + H_2SO_4 \rightleftharpoons HSNO_5 + HNO_3$. In so far as the formation of nitrosulfonic acid is concerned this statement (which has been controverted) is true, but the previous formation of N_2O_3 from the NO and O_2 in the gas space is more doubtful, because nitrogen trioxide does not, except under very special conditions (cf. H. B. Baker and M. Baker)¹ exist as such above -22° , but is dissociated: $N_2O_3 \rightleftharpoons NO + NO_2$. What probably occurs is that a trace of N_2O_3 is formed in equilibrium with NO and NO_2 , and is at once removed by the sulfuric acid, forming the stable nitrosulfonic acid. Whether the N_2O_3 is first produced directly from the NO and O_2 : $4NO + O_2 \rightleftharpoons 2N_2O_3$, or whether the oxidation takes place to NO_2 , which afterwards forms a trace of N_2O_3 by interaction with the excess of NO: $NO_2 + NO \rightleftharpoons N_2O_3$, cannot yet be decided; all that is known is that the oxidation as far as the stage N_2O_3 takes place in a mixture of NO and O_2 far more rapidly than the complete oxidation to NO_2 .²

Lunge's theory is that sulfur dioxide, oxygen and nitrogen trioxide combine directly in presence of a little water to form liquid nitrosulfonic acid, which floats in the chamber as a mist, and this mist, on meeting water floating in the chamber as a mist of dilute sulfuric acid, is decomposed into sulfuric acid and nitrogen trioxide, which acts anew. The reactions are therefore:

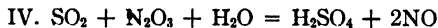
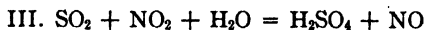


These do not explain the whole mechanism of the chamber process reactions, because in the first chamber dense white fumes are present, and nitric oxide occurs in excess of the proportion

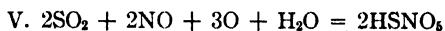
1. J. C. S. 1907, **91**, 1862; abst. C. A. 1908, **2**, 514, 1245; J. S. C. I. 1907, **26**, 1276; Bull. Soc. Chim. 1908, **4**, 968; Chem. Zentr. 1908, **79**, I, 210; Chem. Soc. Ann. Rep. 1907, **4**, 57; Jahr. Chem. 1905-1908, I, 1774; Meyer Jahr. Chem. 1907, **17**, 88.

2. G. Lunge and E. Berl. Zts. ang. Chem. 1902, **15**, 147, 581, 931; 1904, **17**, 1659; 1905, **18**, 60; 1907, **20**, 794, 1713; abst. C. A. 1908, **2**, 303; Zts. ang. Chem. 1906, **19**, 817, 857, 881; abst. C. A. 1907, **1**, 1896. Ber. 1881, **14**, 2196, 1885, **18**, 1384; 1888, **21**, 67, 3264. E. Berl. Zts. ang. Chem. 1910, **23**, 2250; abst. C. A. 1911, **5**, 1323.

NO:NO₂. In this part Lunge thinks that the direct reactions:



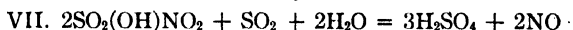
may occur. The NO produced reacts with SO₂ and O₂ present in excess to form nitrosulfuric acid:



Locally, where water is in excess, nitric acid *vapor* may be formed, but this is at once reduced:

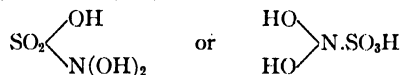


The presence of excess of free NO in the leading chamber is explained as the result of a secondary reaction:

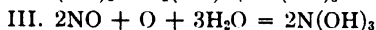
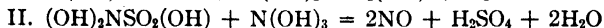
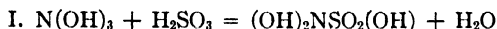


Lunge points out that it is unnecessary to assume N₂O₃ exists in appreciable amounts in the chambers, since nitrous acid and the mixture NO + NO₂ would behave in the same way as N₂O₃.

F. Raschig¹ supposes that the intermediate compound is not nitrosulfonic acid, but a hypothetical dihydroxylamine-sulfuric acid, (OH)₂NSO₂(OH), or



formed when SO₂ and nitrous acid meet, but instantly decomposed by excess of nitrous acid into NO, H₂SO₄, and H₂O. The NO is then reoxidized to nitrous acid, and the process again commences:



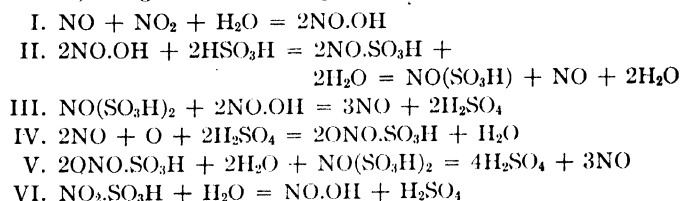
An acrimonious polemic between G. Lunge and F. Raschig followed,² in which hypothetical compounds were multiplied by the latter until his theory hardly contains a single experimental re-

1. Ann. 1887, **241**, 242; **248**, 135; J. S. C. I. 1911, **30**, 1661. Ber. 1907, **40**, 4580; abst. J. S. C. I. 1907, **26**, 1276.

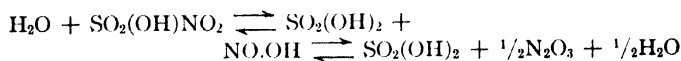
2. G. Lunge and E. Berl. Zts. ang. Chem. 1907, **20**, 711, 1809; Chem. Ztg. 1904, **28**, 1243; abst. C. A. 1908, **2**, 307. G. Lunge, Chem. Ind. 1884, **7**, 5. J. C. S. 1885, **47**, 465. Zts. ang. Chem. 1907, **20**, 2074; abst. C. A. 1908, **2**, 575. F. Raschig, Zts. ang. Chem. 1904, **17**, 1777; 1905, **18**, 1281; 1907, **20**, 694; abst. C. A. 1907, **1**, 1897. J. S. C. I. 1911, **30**, 166; abst. C. A. 1911, **5**, 2912.

action. Lunge's theory has been amplified by Sorel (*Fabr. de l'acid Sulf.*) by taking account of the effect of temperature and dilution of the hydrolysis of nitrosulfonic acid. He lays great stress on the inequalities of temperature in different parts of the chambers. Near the chamber walls the temperature is lower than in the interior. The formation of nitrosulfonic acid is supposed to take place in the interior, where the acid is more concentrated, and the production of sulfuric acid is alleged to take place mainly near the walls, where at the lower temperature, dilution occurs. Convection currents in the gas, set up by the inequalities of temperature, are inferred to cause a spiral motion of the contents of the chambers, which also modifies the reactions. Sorel's theory, while ingenious, is difficult of abstraction.

Another theory of the chamber process has been proposed by M. Trautz,¹ who considers that all the compounds NO, NO₂, HNO₂, HNO₃ and HSNO₃ can act as catalysts in the oxidation of SO₂. He also considers that the compounds NO.SO₃H(nitrosulfonic acid) and NO(SO₃H)₂(nitrosodisulfonic acid) may be formed, and gives the following scheme of reactions:



Much of the supposed complication in the reactions, however, is probably due to the known, but little investigated, reversibility of the reactions:



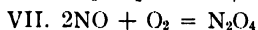
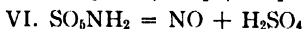
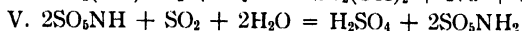
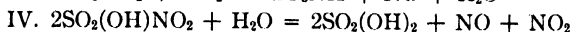
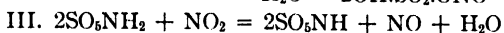
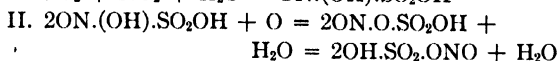
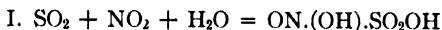
E. Divers² also assumes two catalysts, nitrosulfonic acid and the hypothetical nitrososulfonic acid, ON.SO₃H. G. Lunge³ has

1. Zts. physik. Chem. 1904, **47**, 513; abst. Chem. Centr. 1904, **75**, I, 1301; J. C. S. 1904, **86**, ii, 328; J. S. C. I. 1904, **23**, 440; Bull. Soc. Chim. 1905, **34**, 1217; Rep. Chim. 1904, **4**, 268; Jahr. Chem. 1904, **57**, 457; Tech. Chem. Jahr. 1904, **27**, 83; Wag. Jahr. 1904, **50**, I, 296; Zts. ang. Chem. 1904, **17**, 1552.

2. J. S. C. I. 1904, **23**, 644, 1178; abst. J. C. S. 1905, **88**, ii, 83; Chem. Centr. 1905, **76**, I, 569; Jahr. Chem. 1904, **57**, 458.

3. Sulphuric Acid and Alkali, **1**, 1029.

modified his original theory so as to include a sulfonitronic acid, $\text{ON}(\text{OH})\text{SO}_2\text{OH}$, the formation of which he regards as proved, as an intermediate compound:



Further theories have been advanced by E. Loew,¹ T. Meyer,² C. Engler and J. Weissberg,³ M. Neumann,⁴ S. Littmann,⁵ K. W. Jurisch,⁶ O. Wentzki,⁷ W. Reynolds and W. H. Taylor,⁸ W. Manchot,⁹ E. Briner and A. Kuehne,¹⁰ W. Hempel,¹¹ J. Brode,¹²

1. Zts. ang. Chem. 1900, **13**, 338; abst. J. S. C. I. 1900, **19**, 534; Chem. Centr. 1900, **71**, I, 1040; Jahr. Chem. 1900, **53**, 219; Tech. Chem. Jahr. 1900, **23**, 61; Wag. Jahr. 1900, **46**, I, 327.

2. Zts. ang. Chem. 1901, **14**, 1245; 1902, **15**, 278; abst. J. S. C. I. 1902, **21**, 114; Chem. Centr. 1901, **72**, I, 144, 1079; Jahr. Chem. 1901, **54**, 242; 1902, **55**, 356; Wag. Jahr. 1901, **47**, I, 407.

3. "Kritische Studien über die Vorgänge der Autoxydation," abst. Jahr. Chem. 1904, **57**, 411.

4. Zts. ang. Chem. 1906, **19**, 1702. D. R. P. 169729; abst. Mon. Sci. 1907, **67**, 146; Chem. Centr. 1906, **77**, I, 1637; Chem. Ztg. 1906, **30**, 425; Zts. ang. Chem. 1907, **20**, 264, 974; Jahr. Chem. 1905-1908, I, 1610; Wag. Jahr. 1906, **52**, I, 380. Cf. also G. Lunge, Zts. ang. Chem. 1906, **19**, 1931; 1907, **20**, 267.

5. Zts. ang. Chem. 1906, **19**, 1177; abst. J. S. C. I. 1906, **25**, 694; Chem. Centr. 1906, **77**, II, 1143; Jahr. Chem. 1905-1908, I, 1603; Wag. Jahr. 1906, **52**, I, 388. Compare Erban and Feigensohn, Oest. Chem. Ztg. 1906, 238, 277.

6. Chem. Ind. 1910, **33**, 137; C. A. 1910, **4**, 2715, 3122; abst. Chem. Zentr. 1910, **81**, I, 1943.

7. Zts. ang. Chem. 1910, **23**, 1707; 1911, **24**, 392, 1468; abst. C. A. 1910, **4**, 3122; 1911, **5**, 1322. Compare in this connection, F. Raschig, Zts. ang. Chem. 1907, **20**, 694; 1910, **23**, 2241; C. A. 1911, **5**, 1322. E. Scandola, Zts. ang. Chem. 1911, **24**, 160; abst. C. A. 1911, **5**, 1663.

8. J. S. C. I. 1912, **31**, 365; Chem. Ind. 1910, **33**, 137; abst. C. A. 1910, **4**, 2715.

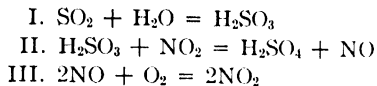
9. Zts. ang. Chem. 1910, **23**, 2112; 1911, **24**, 13; 1914, **27**, 112; Ann. 1910, **372**, 153; **375**, 308; abst. J. S. C. I. 1910, **29**, 563, 1202, 1374; C. A. 1911, **5**, 571. V. Kohlschütter and M. Kutscheroff, Ber. 1904, **37**, 3044.

10. Compt. rend. 1913, **157**, 448; abst. J. S. C. I. 1913, **32**, 941. L. Moser, Zts. anal. Chem. 1911, **50**, 401; abst. J. S. C. I. 1911, **30**, 802.

11. Zts. ang. Chem. 1914, **27**, i, 407; abst. Chem. Zentr. 1914, **85**, I, 2071; see also Zts. Elektrochem. 1906, **12**, 600.

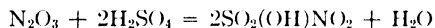
12. Zts. ang. Chem. 1902, **15**, 1081; abst. J. S. C. I. 1902, **21**, 1393; Jahr. Chem. 1902, **55**, 355.

E. Divers,¹ and others,² but the final word has certainly not been said on this perplexing but important question. W. Reynolds and W. Taylor³ revert to the early scheme of reactions:



Recovery of Nitrogen Compounds. The recovery of the nitrogen oxides passing out of the last chamber is a matter of great import in the economical working of the plant, and every effort should be made to ensure that this is done as efficiently as is possible. In some cases this recovery is not as perfect as might be, and losses of niter, the most expensive material used in the process, occur.

The only method in use for the recovery of nitrogen oxides in the chamber process is that proposed by Gay-Lussac in 1827, viz., absorption in concentrated sulfuric acid. This acid does not absorb nitric oxide, but readily takes up nitrogen, N_2O_3 , and N_2O_4 . In the first case the sole product is nitrosulfonic acid, $\text{SO}_2(\text{OH})\text{NO}_2$, which is readily decomposed on dilution with liberation of N_2O_3 , or really a mixture of equimolecular amounts of NO and NO_2 , since N_2O_3 does not exist under the conditions in the denitrators:



This reaction is reversible; when the acid is sufficiently diluted the nitrous fumes are almost completely evolved. The range of concentration over which this occurs is quite narrow, so that

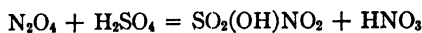
1. J. S. C. I. 1911, **30**, 594; Chem. News, 1911, **103**, 205; abst. Chem. Zentr. 1911, **82**, I, 1894; II, 493.

2. J. Pelouze, Ann. 1846, **60**, 162. S. Hamburger, J. S. C. I. 1889, **8**, 164. F. Hurter, J. S. C. I. 1882, **1**, 52. F. Riedel, Zts. ang. Chem. 1902, **15**, 462, 858. E. Haagen, Zts. ang. Chem. 1902, **15**, 583. G. Keppeler, Zts. ang. Chem. 1902, **15**, 809. M. Trautz, Zts. physik. Chem. 1903, **42**, 513; abst. Chem. Centr. 1904, **75**, I, 1301. A. Mandl and F. Russ, Zts. ang. Chem. 1908, **21**, 486. W. Holweh, Zts. ang. Chem. 1908, **21**, 2131. F. Foerster and M. Koch, Zts. ang. Chem. 1908, **21**, 2161, 2209. M. Bodenstein, Zts. Elektrochem. 1910, **16**, 876.

3. J. S. C. I. 1912, **31**, 367; abst. C. A. 1912, **6**, 2295. Cf. P. Sabatier, Compt. rend. 1896, **122**, 1417, 1479, 1537; **123**, 255; abst. J. S. C. I. 1896, **15**, 616, 662. H. Peterson, D. R. P. 258554, 1912; abst. C. A. 1913, **7**, 2670. A. Nemes, Zts. ang. Chem. 1911, **24**, 3882. Cost systems on sulfuric acid works are described by H. Bush, Chem. Age, 1919, **1**, 58; abst. C. A. 1919, **13**, 2110.

undue dilution is unnecessary in denitrating the sulfuric acid.

In the case of nitrogen dioxide, however, an equivalent of nitric acid is formed with the nitrosulfonic acid, and this is not decomposed by dilution:



It is therefore a disadvantage to have the oxides of nitrogen fully oxidized to NO_2 . In the dilute gas issuing from the chambers, the stage of oxidation does not usually proceed beyond N_2O_3 , especially as a trace of SO_2 is still present. U. Benker¹ and U. Wedge² propose to add a regulated amount of SO_2 to the gases to maintain the nitrogen oxides in the state of N_2O_3 .

Gay-Lussac invented an apparatus for carrying out the absorption, now universally used, and called the Gay-Lussac tower. Although this was described in 1827, it did not come into use until 1842, and was not generally employed until about 1860. The extensive use of the Gay-Lussac tower only became possible when the Glover tower was invented, permitting of a simple denitration of the nitrous vitriol formed in the Gay-Lussac tower.

The Gay-Lussac Tower for the absorption of the nitrous gases consists of resisting material placed at the end of the chamber system, the interior being filled with a packing material exposing a large surface over which fairly concentrated sulfuric acid is distributed. The acid is separated by the packing into small drops, and the gases passing up the tower are divided into a number of separate jets, so that an intimate contact between gas and absorbing liquid is effected. The tall form of the structure is necessary, otherwise it would be impossible to distribute the liquid uniformly over the packing, as channels would be formed which lead to defective absorption. The width must be such as not to impede the draft, and the cubical content is made up in the height of the tower, which is usually about five times the diameter, the tower being square in section. If necessary two or more towers are placed in series, and the gas is then sent to the bottom of one tower, rises through the tower, and is led by mains to the bottom of the second tower. It is not considered good

1. E. P. 1168, 1895; abst. J. S. C. I. 1896, **15**, 197.

2. U. S. P. 1106999; abst. C. A. 1914, **8**, 3354; Zts. ang. Chem. 1916, **29**, 116; Chem. Zts. Rep. 1915, **39**, 114; Mon. Sci. 1914, **31**, 179.

practice to pass gases down a tower in the same direction as the current of absorbing liquid.

The cubical capacity of the Gay-Lussac tower may be taken as at least 1% of the chamber capacity; larger towers being an advantage. In one works, known to the writer, a niter consumption of less than 2% is regularly attained because the Gay-Lussac capacity is unusually ample. For chamber sets of capacity 140,000 to 200,000 cu. ft. the tower may be 6 ft. wide and 50 ft. high; for smaller sets a tower 4 to 5 ft. wide and 40 ft. high may be used. It is advisable to use a somewhat higher tower than these. If sulfur is burnt, and the gases are richer, a tower 30 ft. high is sufficient. An increased Gay-Lussac capacity is, of course, required for intensive working. This may be 2% or 3% of the chamber capacity.

The foundations of the tower may consist of brick or stone piers, or cast-iron pillars with girders to form a platform. These should be well tarred to afford protection from acid, and are covered at the top with sheet lead, having a spout leading the acid drips beyond the brick or iron work. The framework of the tower is usually made with timber, although angle-iron may be used. Circular towers are not uncommon, with a frame of four uprights at the corners of a square, with iron supporting hoops, the timber frame being clear of the lead.

The tower itself is nearly always constructed of lead, 8-lb. being sufficient, with 10-lb. lead for the bottom. A lining of split bricks, put on dry, is sometimes added to prevent the packing bulging the lead, but is unnecessary if the packing is carefully done. The sheets of lead forming the sides should be in one piece from top to bottom, the sides being turned over to overlap the next sheet, to which they are burnt. The overlaps must always be outside, otherwise they are quickly destroyed. This also applies to Glover towers. The bottom consists of a single sheet, with the four edges turned up, the corners being folded. Circular towers are built up of drums, supported by straps. Octagonal towers have been used of volvic stone, without lead shell.

The packing of the Gay-Lussac tower was formerly, and is still largely, graded coke. Patent tower packings have been used for the purpose, and these are described in the next topic.

The advantage of coke is its large surface, and the ease with which it absorbs acid. The best hard-burnt oven coke must be employed, gas coke being useless. It should be of a silvery white color and give a clear ring, being as little porous as possible. Large pieces, about a foot long, are first picked out and laid in at the bottom by hand over the grating at the bottom of the tower, consisting of acid-resisting bricks laid in without mortar. One-third of the tower is packed in this manner. The next third is packed with intermediate pieces, and lastly pieces not less than 3 in. are filled in. Lunge¹ has shown that a slight reduction of nitrous vitriol occurs even with the hardest coke, leading to the formation of NO, which passes out of the tower. In the case of very high towers, one or more grids of iron may be put in to support the weight of the packing.

Owing to the gradual disintegration of the coke packing, it is necessary from time to time to empty and repack the towers, an operation unnecessary if acid resisting special packings, described in the succeeding topic, are used. The cleaning out and repacking of Gay-Lussac towers may, unless carefully conducted, lead to serious danger of poisoning of the workmen, fatalities being recorded. Nitrogen oxides, which are liberated when nitrous vitriol is diluted with water, are very poisonous and dangerous, and especially liable to attack men suffering from cardiac or pulmonary affections. Before beginning the work, the tower must be completely disconnected from the chambers, but the connection with the chimney should be left open. The tower is then washed down first with sulfuric acid and then with water or steam until the liquor running off has a density less than 1.02. While the coke is being taken out the chimney draft must be kept on, when unpacking from the top, the draft should be downwards, and when unpacking from below, the draft should act at the top. If this cannot be done, a large hole should be cut in the side at the bottom. The coke is taken out from the sides as well as from the top, and the coke removed at different levels if the tower is very tall. The workmen should wear respirators and

1. J. S. C. I. 1885, **4**, 31. Zts. ang. Chem. 1890, **3**, 195. See P. Hallwell, Chem. Ztg. 1893, **17**, 263. For precautions in re-packing towers, to prevent fatal poisoning of workmen by nitrous fumes, see Alkali Inspectors Rep. **31**, 90; 1912, **49**, 12. Schubert, Chem. Ztg. Rep. 1912, **36**, 26. Chem. Ind. 1891, **14**, Beilage, p. 30. Chem. Ind. 1904, **27**, 296, 379.

rubber gloves. The mud at the bottom should be stirred up with water until it no longer gives off red fumes, before it is removed. Chloroform is an antidote against nitrous vapors, although oxygen has been recommended in preference.¹

Soc. Anon. des Produits Chimiques de la Manufacture de Javel,² propose to reduce the size of the Gay-Lussac tower by first passing the gases through a special lead-lined tower down which a shower of acid falls on to a layer of coke. H. Petersen³ interposes extra Gay-Lussac and Glover towers, rinsed with acid of about 54° or 55° Bé. and weaker than the usual acids, between the ordinary Gay-Lussac and Glover towers and the chambers. A. Taraud and P. Truchot⁴ wash with water and cool the gases passing from the tower, or treat them with alkaline liquids to free from acid mist. The latter may be removed by chalk, and the nitrous gases then absorbed by alkali. A. Burkhardt⁵ prepares sulfuric acid by bubbling gases containing SO₂ through dilute sulfuric acid so as to charge them with the necessary amount of water vapor, and then through nitrous vitriol. L. Laufer⁶ absorbs the gases not taken out by the Gay-Lussac tower by passing through water, and then recovers. W. Kee and U. Wedge⁷ subject the gases at one or more points between the Glover and

1. K. Reusch, Chem. Ztg. 1911, **35**, 274, 298.

2. E. P. 10871, 1884; D. R. P. 30749; abst. Wag. Jahr. 1885, **31**, 218; J. S. C. I. 1885, **4**, 456.

3. D. R. P. 226793, 1909; abst. C. A. 1911, **5**, 1501; Zts. ang. Chem. 1910, **23**, 2294; Chem. Zentr. 1910, **81**, II, 1345; Jahr. Chem. 1910, **63**, I, 525; Chem. Ztg. Rep. 1910, **34**, 527; Wag. Jahr. 1910, **56**, I, 410; Mon. Sci. 1914, **81**, 87. D. R. P. 208028; abst. Zts. ang. Chem. 1909, **22**, 748; Chem. Zentr. 1909, **80**, I, 1279; Jahr. Chem. 1909, **62**, I, 487; Chem. Ztg. Rep. 1909, **33**, 186; Wag. Jahr. 1909, **55**, I, 337; Mon. Sci. 1912, **77**, 82; Zts. Schiess. Spreng. 1909, **4**, 216. E. P. 27738, 1907; abst. J. S. C. I. 1908, **27**, 981. E. P. 11559, 1907; abst. C. A. 1908, **2**, 308; J. S. C. I. 1907, **26**, 1090. Augt. P. 39350, 1909.

4. E. P. 16866, 1911; abst. C. A. 1913, **7**, 540; J. S. C. I. 1912, **31**, 817. D. R. P. Anm. T-16457. E. P. 9461, 1911; abst. C. A. 1912, **6**, 2826; J. S. C. I. 1912, **31**, 129. U. S. P. 1068021; abst. C. A. 1913, **7**, 2997; Chem. Ztg. Rep. 1913, **37**, 498; Mon. Sci. 1914, **81**, 16. D. R. P. 268815; abst. C. A. 1914, **8**, 1651; Zts. ang. Chem. 1914, **27**, 127; Chem. Zentr. 1914, **85**, I, 505; Chem. Ztg. Rep. 1914, **38**, 37; Wag. Jahr. 1914, **60**, I, 297. D. R. P. 277324; abst. Zts. ang. Chem. 1914, **27**, 566; Chem. Zentr. 1914, **85**, II, 596; Chem. Ztg. Rep. 1914, **38**, 479; Wag. Jahr. 1914, **60**, I, 297. F. P. 425913 and addition 16691 thereto; abst. Chem. Ztg. 1913, **37**, 272.

5. E. P. 29568, 1912; abst. C. A. 1914, **8**, 2040; J. S. C. I. 1913, **32**, 1109.

6. F. P. 481131, 1916; abst. J. S. C. I. 1917, **36**, 136; C. A. 1917, **11**, 2945; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 178.

7. U. S. P. 1220752; abst. C. A. 1917, **11**, 1732; J. S. C. I. 1917, **36**, 547; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 181.

Gay-Lussac towers to the action of an electric discharge. Reversion of nitrogen oxides to their elements is prevented by subjecting them immediately after their formation at the high temperature of electric arcs, to contact with sulfuric acid at a temperature at which it will absorb the oxides. J. Parent¹ introduces cold nitrous vitriol from the Gay-Lussac tower by means of pulsometers into the leading chambers or into two small towers, preferably unpacked, situated between the chambers.²

At the works of the Griesheim Elektron, a centralized method of working the Gay-Lussac towers is used. Seven large sets of chambers are operated, each possessing ordinary Gay-Lussac towers. All of these communicate with a large common tower, 10 ft. by 30 ft. section, in which the nitrous vitriol formed is distributed in the proper amounts to the others.

Working the Gay-Lussac Tower. The main points for attention in the working of this tower are that the gas should be properly oxidized before passing into the tower, since nitric oxide is not absorbed by sulfuric acid; that the gas shall be as cool as possible; and that it shall be dry. The most important point is that the liquid acid used in the tower shall be as cool as possible, since the efficiency of absorption of nitrogen oxides in sulfuric acid of the strength used in the tower, viz., Glover acid of 78% H_2SO_4 , diminishes very quickly with the temperature, much more rapidly than with stronger acid.

The last chamber should receive practically no steam, so that its acid remains at about 106°Tw. , and the gas may be conducted from the chamber to the tower through a long pipe or tunnel, or a special tubular cooler³ interposed between the last chamber and the Gay-Lussac tower.

The acid used in the tower should have a density of at least 144°Tw. ; stronger acid is still more efficient if it can be procured. Acid of 152°Tw. can be obtained from a Glover tower, and this is a suitable strength for use in the Gay-Lussac tower. The acid should be used cool, and may be passed through a refrigerating

1. F. P. 449035, 1911; abst. J. S. C. I. 1913, **32**, 486; Mon. Sci. 1914, **81**, 4.

2. Z. Littmann, D. R. P. 281005, 281537; abst. C. A. 1915, **9**, 1538, 1981; Zts. ang. Chem. 1915, **28**, 82; Chem. Zentr. 1915, **86**, I, 176, 280; Chem. Ztg. Rep. 1915, **39**, 1, 38. R. Cellarius, U. S. P. 848631; abst. C. A. 1907, **1**, 1783. See also Anon., Ind Chim. **11**, 137; abst. C. A. 1911, **5**, 3501.

3. E. Hartmann and F. Benker, Zts. ang. Chem. 1906, **19**, 136.

system before entering the distributing apparatus at the top of the tower. The cooler may consist of a trough of heavy lead, about 2 ft. square, which contains one or two spiral lead coils through which cold water is circulated. The temperature should be reduced to 40° or even less. If there is a sludge valve at the bottom of the tank, mud may be periodically run off.¹

In the ordinary working of the chamber process, at least half the total acid made passes through the Gay-Lussac tower. In some cases the whole of the Glover acid is passed through this tower. In intensive working, double or more the daily production of acid must circulate through the Gay-Lussac tower.

The nitrosity of the acid from the Gay-Lussac tower, which is measured by a nitrometer, should correspond to 1%–2½% N_2O_5 . The acid should be but slightly colored, and have but a faint odor of nitrogen oxides. When mixed with water, especially hot, it should effervesce, and give off red fumes of nitrogen oxides.

The absorption may be controlled by glass sights before and after the tower, the draft being carefully controlled.

Tower Packing. Although coke-packing is still largely used for the Gay-Lussac tower, its tendency to disintegrate and ultimately choke up the apparatus has led to the use, in its place, of a large variety of special packings, mostly of acid-resisting stoneware.

A general discussion of such types of tower packing is given, with data, by "P,"² F. Schobner,³ F. Ludwig,⁴ R. Heinz,⁵ T. Liebig,⁶ H. Petersen,⁷ and J. Partington and L. Parker.⁸ Apart from mechanical requirements such as resistance to crushing weight, convenience in handling and packing, and the obvious

1. W. Crowder, J. S. C. I. 1891, **10**, 300. See also G. Lunge, *Coal, Tar and Ammonia*, 4th Ed. 726. T. Kenyon, E. P. 2491, 1868. K. Kubierschky, E. P. 27496, 1907; abst. J. S. C. I. 1908, **27**, 886. O. Mueller, E. P. 1123, 1911; abst. J. S. C. I. 1911, **30**, 1365. E. P. 28248, 1910. R. Winsloe and B. Hart, E. P. 20143, 1901; abst. J. S. C. I. 1902, **21**, 1183.

2. Gas World, Coking and By-Products Section, 1918, **69**, No. 1772, 15; abst. C. A. 1918, **12**, 2429.

3. Tonindustrietzg. 1913, **37**, 1429; abst. C. A. 1914, **8**, 214. See also F. Zeisberg, Amer. Inst. Chem. Eng. Dec. 1919; Chem. Met. Eng. 1919, **21**, 765; abst. J. S. C. I. 1920, **39**, 143-A.

4. Chem. Appl. 1914, **1**, 271; abst. C. A. 1915, **9**, 258.

5. Zts. ang. Chem. 1906, **19**, 1993; 1913, **26**, 419; abst. C. A. 1907, **1**, 343; 1913, **7**, 3202.

6. Zts. ang. Chem. 1906, **19**, 1806; abst. C. A. 1907, **1**, 225.

7. Zts. ang. Chem. 1911, **24**, 972; abst. J. S. C. I. 1911, **30**, 800.

8. J. S. C. I. 1919, **38**, 75-T; abst. C. A. 1919, **13**, 2109.

necessity that the material shall be acid-resisting, the chief points to be noted in connection with a tower packing material are the surface it presents per cu. ft. occupied by the packing, the surface per cu. ft. total space, the surface per cu. ft. free space (not taken up by material of packing), and the percentage of free space left by the packing. Some types of packing are satisfactory in one or other of these characteristics, but faulty in others. It is necessary to take into consideration all these points in deciding on the merits of a particular packing material, and as many of the articles written on the subject are of an advertising character, they are of little real value. The case for coke packing has been discussed by A. Hutin.¹

A well known type of tower packing is that of O. Guttmann,² which consists of perforated earthenware balls, about 3 in. diameter. While these expose a large surface and take up very little of the capacity, they are exceedingly fragile, and as they are relatively expensive, their use for large towers is almost prohibitive. Many of the balls are usually broken in filling the tower, even with ordinary care, and they also become crushed by the weight of packing above them. Another type of packing devised by O. Guttmann³ is a solid ball, but this sacrifices the small space taken up by the original type, and presents no additional advantages.

A more resistant form of packing is the stoneware ring, or tube, of which modifications have been described by F. Raschig,⁴ who uses small rings from 15 to 50 mm. diameter and height, and with walls 1 mm. thick, which may be heterogeneously placed in the tower so as to lie irregularly; by H. Petersen,⁵ who uses hollow rings having the shape of a regular polygon with an odd num-

1. Rev. Prod. chim. 1918, **21**, 169; abst. C. A. 1919, **13**, 201. See also P. Spence & Sons, Chem. Trade J. **27**, 262.

2. E. P. 14774, 1896. See J. S. C. I. 1898, **17**, 994.

3. E. P. 24847, 1899.

4. E. P. 6288, 1914; abst. J. S. C. I. 1914, **33**, 907; C. A. 1915, **9**, 2433. D. R. P. 286122; abst. Wag. Jahr. 1915, **61**, I, 333; Chem. Ztg. Rep. 1915, **39**, 306; Zts. ang. Chem. 1915, **28**, II, 444. D. R. P. 292622; abst. Wag. Jahr. 1916, **62**, I, 282; Chem. Ztg. Rep. 1916, **40**, 237; Zts. ang. Chem. 1916, **29**, II, 368; J. S. C. I. 1916, **35**, 916. U. S. P. 1141266; abst. J. Gasbeleucht, 1916, 597. Zts. ang. Chem. 1918, **31**, 183; abst. J. S. C. I. 1918, **37**, 677-A. See F. Ludwig, Chem. App. 1915, **2**, 247; abst. C. A. 1916, **10**, 94.

5. E. P. 15406, 1907; abst. J. S. C. I. 1908, **27**, 796. F. P. 378454, 1907; abst. J. S. C. I. 1907, **26**, 1130. D. R. P. 302753, 1913; abst. J. S. C. I. 1918, **37**, 400-A.

ber of sides, and provided with undulating grooves or channels; by J. M. Gibson and the Buckley Brick and Tile Co. (England),¹ who use tubular pieces having on the outer, or inner and outer, surfaces a series of horizontal grooves or channels to hold the liquid; and by the B. Mifflin Hood Brick Co., Atlanta, Ga., who use rings with an internal spiral which serves to mix the gases. Larger rings, stacked in tiers in the towers, may also be used. These are usually about 4 in. high and 4 in. diameter, of resisting stoneware. The drawback to all such types of packing is, in addition to the expense, which, however, is not so great as when balls are used, that they retain practically no acid as compared with porous coke. Intermediate layers of packing and coke may be used to overcome this drawback.²

Ordinary acid-resisting bricks, and a variety of special shaped bricks and blocks, have been used for packing. Accrington Brick & Tile Co. Eng.,³ use channeled packing blocks arranged so as to produce long, narrow, inclined passages. The Ribbertsche Braunkohlen-und Tonwerke⁴ provide the packing blocks on their whole surface with grooves and projections. W. Green and Huncot Plastic Brick & Terra Cotta Co., Eng.,⁵ use layers of bricks or tiles of earthenware or terra cotta, arranged in layers so that the liquid from the outlets in one layer drops into troughs on the top of the next, the blocks being provided with complicated channels on their surfaces for this purpose. J. Harris and D. Thomas⁶ use spaced rows of stepped bricks, some of which rest on projections from the lining of the tower. The packing bricks are stepped at the sides and ends only, and in the latter case have tongues at the upper ends to engage the projections of the lining bricks. S. Wheatley, F. Sheldon and J. Tomlinson⁷ use flat tiles, provided near their ends with projections at opposite sides. The tiles are placed on their sides against each other in superposed rows, and each of the projections has two points of contact with the tile above and below it. G. Lunge and L. Rohrmann⁸ use

1. E. P. 23052, 1900.

2. Farbenfabr. vorm. F. Bayer & Co., F. P. 421952, 1910.

3. E. P. 8152, 1915; abst. J. S. C. I. 1916, **35**, 537.

4. D. R. G. M. 573710.

5. E. P. 28004, 1910; abst. C. A. 1912, **6**, 1506.

6. E. P. 7055, 1915; abst. J. S. C. I. 1916, **35**, 175.

7. E. P. 17472, 1911; abst. J. S. C. I. 1912, **31**, 334.

8. E. P. 6916, 1897. Belg. P. 127142, 1897.

bricks with a central opening surrounded on the upper surface by a rib, and at some distance from this rib another and higher rib, so there is a channel between the two ribs. The under surface is provided with a V-shaped groove surrounding the central slot. Layers of two varieties of these blocks are interposed by layers of plain resisting bricks. H. Nielsen¹ discusses various types of packing, including a form composed of three or more arms or blades radiating from a central boss.

W. Wyld and S. Shepherd,² use bricks or blocks of different widths to form the lining of the tower, so as to leave ledges on which rest strips of glass or other material composing the packing. R. Sauerbrey and A. Wühsche³ use shaped dish-like blocks, with central depressions and connecting channels. W. Oates and E. B. Robinson⁴ employ hollow packing pieces shaped like vases, tapering to both ends, provided with slits, which are stacked in the towers. The lower ends of the sections are open; the upper ends may be open or closed. W. Coxon⁵ lines the tower with acid-resisting tiles, rebated together and kept in place by grooved tie-bricks built into the wall at intervals. The whole is cemented with acid-resisting cement. E. Keller⁶ advocates towers provided with reversely arranged baffles having spiral, radially disposed deflecting blades. L. Boeing⁷ describes a filling composed of shallow dishes arranged in rows one upon another, provided with raised rims having notches. C. Claus⁸ describes the preparation of acid-resisting material from Ganister or Dinas brick, calcined, chilled with water, finely ground, mixed with a small proportion of lime, moulded, dried, and burnt at a high temperature. I. Schlossberg⁹ works up quartzite, colloidal silica and lime, with a flux of glass or ground bricks into a mass from

1. Nitrogen Products and Carbide Co., Ltd., and H. Nielsen, *E. P.* 26269, 1913; *F. P.* 465937. See also *Chem. Trade J.* **54**, 565, 621; **55**, 97. O. Guttman, *Chem. Trade J.* **54**, 671; **55**, 98.

2. *E. P.* 8317, 1907; abst. *J. S. C. I.* 1908, **27**, 492.

3. D. R. P. 158715, 1903; abst. *J. S. C. I.* 1905, **24**, 664.

4. *E. P.* 109915, 1917; abst. *J. S. C. I.* 1917, **36**, 1170.

5. *E. P.* 113015, 1917; abst. *C. A.* 1918, **12**, 1138; *J. S. C. I.* 1918, **37**, 173-A.

6. *U. S. P.* 1247280, 1917; abst. *J. S. C. I.* 1918, **37**, 56-A.

7. *E. P.* 128411, 1899.

8. *E. P.* 4108, 1882.

9. D. R. P. 258683; abst. *Wag. Jahr.* 1913, **59**, I, 577; *Chem. Zentr.* 1913, **84**, I, 1559; *Chem. Ztg. Rep.* 1913, **37**, 231; *Zts. Ang. Chem.* 1913, **26**, 285; *C. A.* 1913, **7**, 2670. D. R. P. Ann. Sch-43938.

which blocks are moulded. These are treated with hydrofluosilicic or hydrochloric acids, the lime salts removed by washing, and the blocks burnt.

• E. Höfling¹ arranges the towers with packing in the form of a spiral staircase, or of pieces of tubing² provided with holes and diaphragms. K. Mescher³ employs perforated plates with spouts which force the gases to change direction. K. Kubierschki⁴ uses wire spirals made up into plates. M. Kypke,⁵ The Friedrichsfeld Ceramic Works⁶ and P. Kestner⁷ also describe stoneware packings.

The packing of towers with Lunge plates⁸ for use as Gay-Lussacs has also proved successful. Lunge recommends the use of plate towers for each set, the exits being combined and led into a large central coke tower. The large amount of acid used for feeding the latter is then distributed among the separate plate towers. In this case the action of the coke on the nitrous com-

1. D. R. P. 272608, 277640; abst. Wag. Jahr. 1914, **60**, I, 293, 294; Chem. Zentr. 1914, **85**, I, 1614; II, 812; Chem. Ztg. Rep. 1914, **38**, 236, 499; Zts. ang. Chem. 1914, **27**, II, 305, 622.

2. D. R. P. 281135; abst. Chem. Zentr. 1915, **86**, I, 177; Chem. Ztg. Rep. 1915, **39**, 2; Zts. ang. Chem. 1915, **28**, II, 83; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110; Wag. Jahr. 1915, **61**, I, 212.

3. D. R. P. 259764; abst. Wag. Jahr. 1913, **59**, I, 510; Chem. Ztg. Rep. 1913, **37**, 330; Zts. ang. Chem. 1913, **26**, 357; C. A. 1913, **7**, 3051.

4. D. R. P. 259362; abst. Wag. Jahr. 1913, **59**, I, 654; Chem. Ztg. Rep. 1913, **37**, 318; Zts. ang. Chem. 1913, **26**, 316; C. A. 1913, **7**, 3051.

5. D. R. P. 97208; abst. Wag. Jahr. 1898, **44**, 327; Chem. Centr. 1898, **69**, II, 514; Zts. ang. Chem. 1898, **11**, 588.

6. O. Franz and Deutsche Steinzeugwaarenfabrik, D. R. P. 89025; abst. Wag. Jahr. 1896, **42**, 1144; Chem. Ztg. 1896, **20**, 974.

7. E. P. 131502; abst. J. S. C. I. 1919, **38**, 764-A. Cf. P. Gilchrist, U. S. P. 527680, 1894.

8. See F. Lütty, Zts. ang. Chem. 1897, **10**, 485. H. Niefenführ, Chem. Ztg. 1897, **21**, 176. H. Petersen, Zts. ang. Chem. 1911, **24**, 972; abst. J. S. C. I. 1911, **30**, 800. S. Kohn, Chem. Ztg. 1907, **31**, 758; abst. C. A. 1907, **1**, 2817. See also L. Deruelle, U. S. P. 578548, 1897. F. Moore and J. Hall, Acid Condenser, U. S. P. 986846. U. Wedge, Condenser for Vapors and Gases, U. S. P. 1012487. O. Eliel, Apparatus for manufacturing sulfuric, U. S. P. 725427. Material for filling sulfuric acid towers, C. Heinz, Chemical Engineer, July 1916, p. 113. C. Graham, Tower for condensing acid, U. S. P. 436414. G. Hänisch, Boiling and precipitating tower, U. S. P. 477755. G. Lunge, Apparatus for treating liquids with gases, U. S. P. 485126. E. Barbier, Process and apparatus for making sulfuric, U. S. P. 535882. N. Pratt, Process and apparatus for making sulfuric, U. S. P. 546596. R. Scherfenberg, Structure made of bricks for reaction towers, U. S. P. 888120. H. Petersen, Filling for reaction chambers, U. S. P. 899898 and U. S. P. 899899. O. Guttman, Filling material for reaction spaces, U. S. P. 912310. W. Hommel, Liquid distributors for absorption towers, E. P. 19668, 1908. O. Niefenführ, Filling for reaction towers, D. R. P. 216342. H. Vollberg, Filling bodies for reaction towers, D. R. P. 247950. R. Moritz, Columns for absorption and reaction towers, F. P. 462877. C. Scheer & Co., Purification of gases in reaction tower, Aust. P. 40901.

pounds is insignificant, on account of the low temperature and the small percentage of nitrous compounds in the acid.

Distributing the Feed Acid. The importance of evenly distributing the feed acid over the packing of the tower has already been emphasized. Many devices have been used for this purpose, as the so-called Acid Wheel, devised by Schaffner. In the top of the tower there are 16 holes, through which acid trickles down on the packing. Each hole has a rim about $1\frac{1}{4}$ in. high, covered with a lead cap serrated at the edges to a depth of $\frac{3}{4}$ in. As soon as the tray is filled with acid, the latter runs through the holes into the tower, and gas cannot escape on account of the acid seal. The spreading of the acid is effected by a small reaction wheel supplied from a tank with a tap regulating the feed. The lower part of the wheel and the two arms are of lead, into which is fixed a strong glass tube above, and a short glass tube below, drawn out to a point running in a socket of glass or lead, one of the arms carrying a glass tube from which acid discharges. A guide, consisting of two parallel rods of glass or lead, rests on frames fitting into the slots, and carrying four crossed glass tubes forming a square, inside which the upright tube revolves. The axle of the wheel is exactly in the center of the tower, and a lead cylinder 4 in. high is burnt on beneath. From this radiate 16 lead ledges burnt to the top lead, and branching off at equal distances. Beyond an imaginary circle, representing the maximum distance which the rotor throws acid, these lead strips change direction, so that each of the 16 holes comes between two strips.

Instead of using wheels, which sometimes stop, an overflow arrangement may be applied, in which the liquid runs into a central vessel provided with a loose cover. From this vessel, which is serrated at the bottom, the acid runs into a trough provided all round its circumference with spouts, as many as 30 or 40 of which may be used, and must discharge equally. The trough is surrounded by a wider trough divided into as many cells as there are spouts. Each cell is independent, but partitions are cut out on the top so as to permit overflow in case of stoppage. Each cell has a luted discharge pipe covered with a cap.

Other types of distributor have been described by F.

Briegleb,¹ J. Brock and E. Saye,² W. Hömmel and the Metals Extraction Corporation,³ F. Klute and H. Ising,⁴ and Farbenfabrik vorm. F. Bayer & Co.⁵

T. Briggs⁶ uses a conical distributor, fluted outside, below which is a perforated disc, the holes in which correspond with the outlets of the distributor. C. Fowler and E. Medley,⁷ cause the liquid to run from the outside to the center, where it is atomized by revolving discs. A new feeding device is described by the Steinzeugwarenfabrik f. Canalisation in Friedrichsfeld;⁸ it has no revolving parts, and only one opening in the top of the tower is required. H. Pauling⁹ uses an intermittent spreader, fed from above and having a spray below. The spread of the spray is gradually diminished as liquid empties, so that all the parts of the tower section are wetted. W. Noll¹⁰ also describes spraying apparatus.

The regularity of the acid supply is important, and this cannot be secured by simply emptying it from a tank, as the velocity of flow then decreases with the fall of head of liquid in the tank. A mechanical feed apparatus may be used, one type consisting of a vessel placed mouth downwards in a trough so that its mouth is hydraulically luted. As acid empties, the neck is opened, and acid runs out.

The balancing type of apparatus is also used. In this a large lead-lined tank on the top of the tower is periodically filled. A lead cylinder 12" wide, communicates with the bottom of the tank through a lead tube which has a valve-seat of hard lead. The valve-seat is covered by a ball of hard lead with a guide rod.

1. D. R. P. 10386; abst. Wag. Jahr. 1880, **26**, 229; J. A. C. S. 1880, **2**, 377.
2. E. P. 11492, 1885; abst. J. S. C. I. 1886, **5**, 487.
3. E. P. 19668, 1908; abst. J. S. C. I. 1909, **28**, 1112; Chem. Ztg. Rep. 1910, **34**, 170.
4. D. R. P. 209276; abst. Chem. Zentr. 1909, **80**, I, 1620; Jahr. Chem. 1909, **62**, I, 386; Chem. Ztg. Rep. 1909, **33**, 278; Wag. Jahr. 1909, **55**, I, 610.
5. D. R. P. 241767; abst. C. A. 1912, **6**, 2152; Zts. ang. Chem. 1912, **25**, 126; Chem. Zentr. 1912, **83**, I, 171; Chem. Ztg. Rep. 1912, **36**, 27; Wag. Jahr. 1911, **57**, I, 653.
6. U. S. P. 1032657; abst. C. A. 1912, **6**, 2676.
7. E. P. 23864, 1911; abst. C. A. 1913, **7**, 1311; J. S. C. I. 1912, **31**, 1167; Chem. Ztg. Rep. 1913, **37**, 192.
8. Described in Met. Chem. Eng. 1911, **9**, 613; abst. C. A. 1912, **6**, 414.
9. E. P. 22321, 1910.
10. D. R. P. 276663; abst. Zts. ang. Chem. 1914, **27**, 536; Chem. Ztg. Rep. 1914, **38**, 443; Wag. Jahr. 1914, **60**, I, 598.

above of the same metal, which is operated by a chain from a balance arm swinging on a steel edge. The other side of this arm carries a float dipping into the acid. The level of this acid, and therefore the rate of efflux, are thus kept constant. The *Semper idem* apparatus, made by the Vereinigte Tonwaarenwerke, Charlottenburg, employs a floating siphon, carried by a bell.

Pumping the Acid. On account of the height of the Gay-Lussac towers, it is necessary to force the acid from the Glover tower, where it is concentrated, to the top of the Gay-Lussac tower by means of special pumps or acid elevators. The material of which these pumps is constructed must resist the action of sulfuric acid of the concentration in which it is produced in the Glover tower; such materials being lead, cast-iron and stoneware.

The oldest method of lifting the acid, and one which is still largely used, is by means of *acid-eggs*, or *montejus*, which are closed vessels containing acid and provided with a lift-pipe, or tube reaching to the top of the Gay-Lussac tower, an inlet pipe for acid, and an air-pipe, through which compressed air from a blowing-engine is admitted and forces the acid from the egg to the required place.

The dimensions of the blowing engine vary according to the size of the plant; for a set of chambers of 140,000 to 200,000 cu. ft. capacity a steam cylinder of 8 in. diameter, an air cylinder of 12 in. diameter, a stroke of 18 in., with 40 to 60 r. p. m. are sufficient. In this case the air is delivered through a $1\frac{1}{4}$ - $1\frac{1}{2}$ in. pipe. To prevent acid being carried back to the pump, and corroding the valves, the lead air pipe is carried upwards for 10-13 ft. and then downwards to the egg. A small cock is soldered on near the pump, to relieve air pressure when the pumping is finished.

The original type of acid egg was a cast-iron vessel with a lead lining. Horizontal cylinders with bolted covers are more convenient, but the latest pattern is a horizontal cylinder with one semi-circular and one neck-shaped end, the latter closed by a manhole cover. These vessels need not be lined with lead. Stoneware acid eggs are shaped like Woulfe bottles, with three necks, and are made of very thick and strong ware.

In the acid tanks the pressure valve consists of a cylinder of strong lead, communicating with the tanks by pipes ending in

the bottoms of the tanks in valves of regulus metal operated by lead-covered handles. When acid is to be run from the tanks to the egg the valve in the tank is opened, the bottom valve also being open, and operated by a lead-covered rod, ending above in a screw turned by a hand wheel. The rod and wheel are carried by a very strong iron frame bolted to the bottom joists. When the vessel is full of acid, the valve is screwed down tightly by the wheel, and the stopper is put in the tank seating. The acid may now be raised from the egg to the top of the tower by compressed air. When the egg is blown out, the air pressure is released, the vessel being emptied by gravity into the egg.

Harrison Blair's self-acting egg consists of a valve box and the delivery pipe, into which a tube enters a little above the egg. When the vessel is full, the escape of air is stopped by the liquid, which is forced upwards, and which, acting as a siphon, stops the passage of air.

A pulsometer may also be used for raising acid, which usually consists of a cast-iron vessel filled from a supply tank by a pipe containing a non-return valve. The compressed air is admitted and the acid raised through a pipe. During the filling of the vessel the air escapes through apertures. A. Simon¹ uses two pulsometers. The pulsometer apparatus has been considerably improved by P. Kestner,² who replaced the siphon by a float valve. Kestner's elevators have been largely used instead of acid eggs. The recent type of apparatus is constructed of cast-iron. The acid runs in from a tank placed at an elevation, through a valve into an elevator. When this is filled the acid raises a float which operates by a rod on a valve, at the same time shutting the outlet valve so that air forces the acid up the exit pipe. Part of the compressed air enters when all the liquid has been driven out, and owing to the diminution of pressure, the float descends, opening the air outlet and closing the air inlet. Different modifications of this very successful apparatus have been devised.

Acid elevators have been described by the Deutsche Steinzeugwarenfabrik, of Friedrichsfeld,³ P. Schütze of Oggersheim,⁴

1. Zts. ang. Chem. 1890, **3**, 356; abst. Wag. Jahr. 1890, **36**, 591.

2. J. S. C. I. 1903, **22**, 337; Chem. Ztg. 1910, **34**, 734. See also O. Guttmann, J. S. C. I. 1903, **22**, 1333; Zts. ang. Chem. 1903, **16**, 915.

3. D. R. P. 145599, 145600; abst. Chem. Ind. 1905, **25**, 432. A.

4. Described by A. Innerhofer, Eng. Min. J. **90**, 330; abst. C. 1910, **4**, 2715.

G. Plath and the Deutsche Ton-und Steinzeugwerke of Charlottenberg,¹ C. Scherb,² the Badische Co.³ and T. Meyer.⁴ The latter used centrifugal pumps,⁵ and states that a considerable amount of power is wasted in compressed air elevators. Acid pumps have been detailed by R. Moritz,⁶ and A. Ferraris.⁶ The "Mammoth pump" elevator is described by A. Borsig,⁷ and C. Nagelschmidt⁸ has patented an arrangement for avoiding splashing when elevators are used. The general question of raising liquids is discussed by Deimler⁹ and others.¹⁰

The Glover Tower. The recovery of the nitrogen compounds in the chamber system was only possible on an extended scale after the invention of the Glover tower, since, although with the Gay-Lussac tower it is possible to absorb the nitrogen oxides from the exit gases, so long as there was no convenient means of returning these gases into the system, this step was but of little use.

The Glover tower was invented by John Glover, an acid manufacturer of Newcastle, England, in 1859.¹¹ At first the use

1. D. R. P. 159079; abst. Wag. Jahr. 1905, **51**, I, 548; Zts. ang. Chem. 1905, **18**, 749; Chem. Zts. 1905, **4**, 388. Cf. also Zts. ang. Chem. 1907, **20**, 1186.

2. E. P. 10051, 1907.

3. D. R. P. Anm. B-60169.

4. Zts. ang. Chem. 1910, **23**, 1556; abst. C. A. 1909, **3**, 2982.

5. F. P. 441304, 1912; abst. C. A. 1913, **7**, 404.

6. E. P. 4482, 1914; abst. J. S. C. I. 1915, **34**, 263. F. P. 457936.

7. Chem. Ztg. 1914, **38**, 274.

8. D. R. P. 279074; abst. J. S. C. I. 1915, **34**, 227; C. A. 1915, **9**, 1231.

9. Chem. Ind. 1911, **34**, 39.

10. Anon., Met. Chem. Eng. 1911, **9**, 161; abst. C. A. 1911, **5**, 1663. Anon., Min. Sci. Press, **102**, 386; abst. C. A. 1911, **5**, 2418. R. Bithel and C. Beck, E. P. 28743, 1913. G. Clifford, Iron Age, 1914, **94**, 945; abst. C. A. 1915, **9**, 128. G. Davis, E. P. 15459, 1912. Kirchofer, D. R. P. 262464. J. Dye and W. Lucas, U. S. P. 1249728, 1917; abst. J. S. C. I. 1918, **37**, 88-A. O. Maas, Can. Chem. J. 1918, **2**, 195; abst. C. A. 1918, **12**, 2663. Pauling, D. R. P. 242515. W. Strzoda, E. P. 26732, 1913; abst. J. S. C. I. 1914, **33**, 643. F. Tschudy, U. S. P. 1135471, 1915; abst. J. S. C. I. 1915, **34**, 611. S. Tungay, Chem. Age, 1919, **1**, 326; abst. J. S. C. I. 1919, **38**, 716-A; C. A. 1919, **13**, 3285.

11. In this connection see G. Lunge, Dingl. Poly. 1871, **201**, 341; **202**, 532; 1875, **215**, 56; **216**, 79; 1877, **225**, 474; Ber. 1877, **10**, 1432. F. Bode, Dingl. Poly. 1871, **202**, 448; J. McCulloch, Chem. News, 1873, **27**, 135. J. Glover, Chem. News, 1873, **27**, 152. G. Lunge, Chem. News, 1873, **27**, 162. M. Vorster, Dingl. Poly. 1874, **213**, 506. F. Hurter, Dingl. Poly. 1878, **227**, 465, 563. G. Lunge, Dingl. Poly. 1878, **228**, 70, 152. F. Bode, Dingl. Poly. **217**, 305. Bräuning, Zts. J. Bergwesen, 1877, 140. See also K. Jurisch, "Schwefelsäurefabrikation," 153. Chem. News, 1875, **31**, 85. For the life and work of John Glover, see J. Dunn, J. S. C. I. 1903, **22**, 1177.

of the tower, which was never patented* by Glover, met with great opposition, but ultimately has been universally adopted in all chamber plants. In the old plants, no less than 10-15 lbs. of niter were used for every 100 of sulfur burnt, a proportion which has been reduced to less than 2 in the best works, and to an average of 3, and has been only possible with the complete denitration effected by the Glover tower. Instead of decomposing the nitrous vitriol from the Gay-Lussac tower with water or steam, as previously had been done, Glover effected the decomposition by a mixture of steam and sulfur dioxide obtained by passing the burner gas through the tower down which weak chamber acid and nitrous vitriol flowed. In this manner all the nitrous compounds were recovered and passed into the chamber, and in addition the weak acid was concentrated in two ways. First by evaporation by the hot burner gases, which were cooled to the point necessary for use in the chambers, and secondly by the actual production of sulfuric acid in the tower itself:



About 25% of the total acid made is estimated to be produced in the Glover tower, with a great saving of chamber space. The importance of this apparatus is thus evident.

The general construction of the Glover tower consists of an outer shell of lead, lined with acid-resisting material put in without mortar, and packed with flints, or other suitable acid-resisting packing. There is an inlet below for the burner gas from the ore burners, and an outlet above to the chambers. At the top are storage tanks for chamber acid and nitrous vitriol, which are run down the tower in regulated amounts. The concentrated acid, completely freed from nitrous compounds, runs from the bottom of the tower to coolers.

The lining of the tower may be volvic lava, from Pûy-de-Dôme, which is very resisting, but expensive, or special bricks or blocks, of which a variety are on the market. In England, "blue bricks" from Flintshire are largely used;¹ in Germany bricks made at Bad Neuheim, Bendorf, and Aussig. The clay from which such bricks are made should² be richer in silica than alumina,

1. Made by the Buckley Brick & Tile Co., see Chem. Trade J., **10**, 46.
2. Tonindustrieltg. 1890, 642.

and free from iron. An artificial mixture consists of 25 to 30 parts of feldspar, 25 to 30 of china clay, and 40 to 50 of quartz, burnt to a clinker. The bricks may then be glazed with a mixture of 54 parts quartz, 84 of feldspar, 35 of ground chalk, and 26 of ground china clay. J. Skoglund¹ mixes quartz powder with sodium silicate, and treats with sulfuric acid, which removes alkali. The mass is applied in a layer $\frac{1}{2}$ in. thick, and dried by a fire-heat. "Obsidianite"² appears to be a similar mixture. A. Karyscheff³ produces acid-proof bricks from powdered spinel, chromite, etc., agglomerated by cement under great pressure. G. Nichols, W. Nichols and J. Herreshoff⁴ pack the tower with rough quartz blocks without a special lining, filling in the space between these and the lead with finely crushed quarts or glass. M. Walsh⁵ uses cut quartz blocks for the lining; vitreosil might also be used, but is a very fragile material.

The foundation of the tower may consist of brick pillars, with a roof consisting of a strong brick arch, with iron tie-rods. The top is covered with a lead apron of 6-7 lb. weight, to protect against acid drips, turned up to form a saucer. Between this and the bricks, a layer of pitch may be placed. The frame of the tower is usually of wood, preferably of pitchpine, but iron frames may be employed. The frame is required to support the acid tanks at the top of the tower, enclosed in a light covering shed.

The tower itself is made from 14-lb. lead, the bottom being of 35-lb. lead, and the straps of 9-lb. It is suspended in the same way as the chambers. Circular towers are also used, the sections being made as drums, and burnt together. The bottom saucer of the tower is formed of two sheets of lead joined in the center, and turned up all round to a height of a foot. The burning is carried out by cutting away the adjacent edges slantingly, and pouring melted lead from a ladle into the grooves, running over with a red-hot iron.

Provision is made for keeping the saucer cool by air channels

1. U. S. P. 640037; abst. Mon. Sci. 1905, **63**, 747.
2. Chem. Trade J. 1909, **44**, 181; 1912, **50**, 70.
3. E. P. 2994, 1907; abst. J. S. C. I. 1908, **27**, 506. F. P. 350016, 1904; abst. J. S. C. I. 1905, **24**, 971.
4. E. P. 1861, 1886; abst. J. Soc. Dyers Col. 1886, **2**, 48; Wag. Jahr. 1886, **32**, 262. See also C. Chandler, J. S. C. I. 1908, **27**, 269.
5. E. P. 1486, 1884; abst. J. S. C. I. 1884, **3**, 260; U. S. P. 292078; abst. Wag. Jahr. 1884, **30**, 299; J. A. C. S. 1884, **6**, 53.

in the supporting brickwork. The lip of the saucer from which the acid runs, is exposed to great wear, and a loose false lip is put over it, which may be renewed as required.

The lead top of the tower is suspended from wooden or iron rails by lead straps, and is dished in the center so that acid leaks from the tanks find their way through the hydraulic seal of the tower distributor.

The gas inlet and outlet of the tower are important. The outlet is of lead pipe, set with a slight upward slope near the tower, rising a little towards the chamber, so that acid may run back to the tower. The inlet pipe is usually made from cast-iron, and is fitted to the tower by the following arrangement: The pipe is bolted to a metal casting in two parts which form a ring, the space being caulked with iron filings, sulfur and sal ammoniac. In the side of the tower a circular hole is cut, to which a flange is burnt, fitting the outer circumference of the iron ring. Between the lead and iron a little cement of fire-clay and tar is placed, and the lead, cement, and cast-iron are bound with an iron hoop. Another method, used at Griesheim, consists of a burner pipe enlarged at its end so as to fit over a dry-walled annular brick flue, while the other end of this flue is held in the brick lining of the tower. The lead of the tower is continued in a lead cylinder, a flange of which is bolted to the iron flange.

The tower lining is thicker, say 2 ft. 3 in., at the bottom, while at 4 ft. above it may diminish to 18 in. The recess formed serves as a support for stone slabs carrying the packing. Higher up the lining thins down to 14 in., and finally to 9 in. The whole lining, as well as the lower arch, is put in without mortar, and moulded blocks are convenient for this purpose. It may last three years without renewal.

The packing of the tower varies greatly. In English works¹ quartz blocks are mostly used, although special packings are often employed. Rings and blocks of the most varied types have been described, some of which have been mentioned in connection with the Gay-Lussac tower (p. 1262). Varieties specially suitable for packing the Glover tower have been advocated by

1. Alkali Insp. Rep. 1915, **52**; abst. J. S. C. I. 1916, **35**, 1011.

D. Knab,¹ J. Saunders,² H. Klencke,³ F. Lütty,⁴ R. Sauerbrey and A. Wünsche,⁵ H. Rabe,⁶ R. Evers,⁷ H. Wilisch,⁸ J. Mackenzie and J. Gibson,⁹ the Vereinigte Damfziegeleisen-Industrie, A. G. Berlin,¹⁰ the Chemische Fabrik Griesheim-Elektron,¹¹ E. Peyton,¹² A. Wilhelmi,¹³ E. Steinbrecht,¹⁴ R. Scherfenberg,¹⁵ H. Petersen,¹⁶ W. Green and the Huncoat Brick and Terra Cotta Co.,¹⁷ O. Niedenführ,¹⁸ W. Wyld and S. W. Shepherd,¹⁹ O. Guttman,²⁰ R. Pav-

1. D. R. P. 67085; abst. Zts. ang. Chem. 1893, **6**, 231; Wag. Jahr. 1893, **39**, 373; Ber. 1893, **26**, 457; Mon. Sci. 1894, **44**, 922.

2. U. S. P. 144928, 1873.

3. E. P. 25027, 1909; abst. J. S. C. I. 1910, **29**, 564. Belg. P. 214844, 1909. Metallbank u. Metallurgische Ges., D. R. P. 284995, 1913; abst. J. S. C. I. 1915, **34**, 1091; Zts. ang. Chem. 1915, **28**, 364; Chem. Zentr. 1915, **86**, I, 215; Chem. Ztg. Rep. 1915, **39**, 253. D. R. P. 219400, 1908; abst. C. A. 1910, **4**, 2032; Zts. ang. Chem. 1910, **23**, 1052; Chem. Zentr. 1910, **81**, I, 970; Jahr. Chem. 1910, **63**, I, 525; Chem. Ztg. Rep. 1910, **34**, 159; Wag. Jahr. 1910, **56**, I, 412; Mon. Sci. 1913, **79**, 159; Zts. Schiess. Spreng. 1910, **5**, 174.

4. Zts. ang. Chem. 1896, **9**, 645.

5. D. R. P. 158715; abst. Wag. Jahr. 1905, **51**, I, 533; Zts. ang. Chem. 1905, **18**, 750.

6. Zts. ang. Chem. 1904, **17**, 78; 1906, **19**, 708. D. R. P. 148205; abst. Zts. ang. Chem. 1904, **17**, 628; Chem. Ztg. 1904, **28**, 389; Wag. Jahr. 1904, **50**, I, 516; Chem. Zts. 1904, **3**, 685.

7. D. R. P. 172678; abst. Chem. Ztg. Rep. 1906, **30**, 270; Zts. Schiess. Spreng. 1906, **1**, 260.

8. D. R. P. 173612; abst. Chem. Zts. 1907, **6**, 23; Chem. Ztg. Rep. 1906, **30**, 281; Wag. Jahr. 1907, **53**, I, 586; Zts. Schiess. Spreng. 1906, **1**, 320.

9. E. P. 17832, 1906; Chem. Trade J. 1908, **42**, 535; abst. J. S. C. I. 1907, **26**, 395.

10. D. R. P. 191890; abst. Chem. Ztg. Rep. 1908, **32**, 3; Wag. Jahr. 1908, **54**, I, 581; Chem. Zts. 1908, **7**, 616.

11. D. R. P. 218779; abst. Chem. Zentr. 1910, **81**, I, 875; Jahr. Chem. 1910, **63**, I, 416; Chem. Ztg. Rep. 1910, **34**, 125; Mon. Sci. 1913, **79**, 158.

12. E. P. 18831, 1908; abst. J. S. C. I. 1909, **28**, 828.

13. D. R. P. 219759; abst. Chem. Zentr. 1910, **81**, I, 1073; Jahr. Chem. 1910, **63**, I, 416; Chem. Ztg. Rep. 1910, **34**, 170.

14. D. R. P. 236880; abst. C. A. 1911, **5**, 3614; Zts. ang. Chem. 1911, **24**, 1534; Chem. Zentr. 1911, **82**, II, 314; Wag. Jahr. 1911, **57**, I, 652; Chem. Ztg. Rep. 1911, **35**, 432. D. R. P. Anm. A-12244.

15. D. R. P. 184893; abst. Chem. Ztg. Rep. 1907, **31**, 271; Wag. Jahr. 1907, **53**, I, 586; Zts. Schiess. Spreng. 1907, **2**, 236. E. P. 4366, 1907; abst. J. S. C. I. 1907, **26**, 955. D. R. P. 239072; abst. C. A. 1912, **6**, 2149; Zts. ang. Chem. 1911, **24**, 2179; Chem. Ztg. Rep. 1911, **35**, 555; Wag. Jahr. 1911, **57**, I, 652.

16. F. P. 382262. D. R. P. 209681; abst. Chem. Zentr. 1909, **80**, I, 1679; Jahr. Chem. 1909, **62**, I, 487; Chem. Ztg. Rep. 1909, **33**, 319.

17. E. P. 28004, 1910; abst. C. A. 1912, **6**, 1506; J. S. C. I. 1911, **30**, 1380; Chem. Ztg. Rep. 1912, **36**, 287.

18. D. R. P. 183748; abst. Chem. Ztg. Rep. 1907, **31**, 234; Wag. Jahr. 1907, **53**, I, 586. D. R. P. 216342; abst. Chem. Ztg. Rep. 1910, **34**, 3.

19. E. P. 19001, 1906; abst. J. S. C. I. 1907, **26**, 859.

20. E. P. 4407, 1907; abst. J. S. C. I. 1907, **26**, 859.

litzek,¹ S. Wheatley, F. Sheldon and J. Tomlinson,² E. Hocfling,³ J. Harris and D. Thomas,⁴ E. Berl and A. Innes,⁵ F. T. Tone and the Carborundum Co.,⁶ I. Moscicki,⁷ H. Vollberg,⁸ K. Hulett,⁹ and P. Kestner.¹⁰

Usually the tower is not completely packed; the temperature of the gas leaving the tower should be 60°-75°, otherwise too much steam returns by condensation.

The Glover tower should not be higher than 20 to 25 ft.; increased capacity is obtained by enlarging the diameter. The fixed height is due to the necessity of having a proper gradation of the zones of temperature.

The distribution of the acids at the top is carried out as described in connection with the Gay-Lussac tower, the cubic capacity of which, according to Lunge, should be 550 cu. ft. per ton of sulfur burnt per 24 hours.

Circular or polygonal towers are used in some cases; the circular forms require no supporting stays and less lead, and have no sharp corners. They are much less easy to build than square towers and require shaped linings. Volvic lava towers, with a thin outer lead shell to prevent leakage, have been used;¹¹ and towers without lead have been described.¹²

Designs of modern Glover towers have been given by F.

1. D. R. P. 229999; abst. C. A. 1912, **6**, 278; Zts. ang. Chem. 1910, **23**, 276; Chem. Ztg. Rep. 1911, **35**, 83; Wag. Jahr. 1911, **57**, I, 651.
2. E. P. 17472, 1911; abst. J. S. C. I. 1912, **31**, 334.
3. D. R. P. 281135, 1912; abst. J. S. C. I. 1915, **34**, 611; Zts. ang. Chem. 1915, **28**, 83; Chem. Zentr. 1915, **86**, I, 177; Chem. Ztg. Rep. 1915, **39**, 2¹; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110.
4. E. P. 7055, 1915; abst. J. S. C. I. 1916, **35**, 175; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110. Accrington Tile Co., E. P. 8152, 1915; abst. J. S. C. I. 1916, **35**, 537; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110.
5. D. R. P. 263200; abst. C. A. 1913, **7**, 3863; Zts. ang. Chem. 1913, **26**, 508; Chem. Zentr. 1913, **84**, I, 826; Chem. Ztg. Rep. 1913, **37**, 514; Wag. Jahr. 1913, **59**, I, 505.
6. Met. Chem. Eng. 1913, **11**, 103.
7. E. P. 17355, 1911; abst. C. A. 1913, **7**, 393; J. S. C. I. 1912, **31**, 801.
8. D. R. P. 247950; abst. C. A. 1912, **6**, 2827; Zts. ang. Chem. 1912, **25**, 1698; Chem. Zentr. 1912, **83**, II, 207; Chem. Ztg. Rep. 1912, **36**, 416; Wag. Jahr. 1912, **58**, I, 653.
9. K. Hulett and Chandler, Ltd., S. Hersey and E. Blake, E. P. 18129, 1908; abst. J. S. C. I. 1909, **28**, 873. E. P. 23813, 1911; abst. C. A. 1913, **7**, 1311; J. S. C. I. 1912, **31**, 801; Chem. Ztg. Rep. 1913, **37**, 192.
10. E. P. Appl. 17065, 1918; J. S. C. I. 1918, **37**, 675-A.
11. O. Guttmann, J. S. C. I. 1908, **27**, 667.
12. Steuler & Co., D. R. P. 227283; abst. Wag. Jahr. 1910, **56**, I, 425.

Lüty,¹ H. Nidenführ,² and F. Lüty and H. Nidenführ.³ The use of a fan to regulate the draft through the chamber system has been described by H. Nidenführ,⁴ who divides the functions of the Glover tower between two towers, and places a fan between them. The burner gases pass through the first concentrating Glover, where they give up most of their heat, and are purified from dust. The purified and cooled gases are then forced by a fan through the second denitrating Glover, from which they pass to the chambers. Nitrous vitriol from the Gay-Lussac, together with sufficient steam and chamber acid to reduce the gravity to 1.619, or not more than 1.65, are fed to the denitrating Glover. The issuing acid still contains nitrogen acids equivalent to 0.2% nitric acid of sp. gr. 1.33. It is run into the concentrating Glover, where all traces of nitrous compounds are removed and the gravity brought up to 1.71-1.73. In this way the work of the burners is made independent of that of the chambers.

Special arrangements of the Glover tower, and methods of operating the same, have been described by L. Rohrmann and H. Nidenführ,⁵ R. Bithell and J. A. Beck,⁶ F. Curtius & Co.,⁷ J. Parent,⁸ H. Hegeler and N. I. Heinz,⁹ W. Quinan,¹⁰ the Aktien-Gesellschaft für Bergbau, Blei-und Zinkfabrikation,¹¹ J. Lüttgen,¹²

1. Zts. ang. Chem. 1896, **9**, 640; 1897, **10**, 490.

2. Chem. Ztg. 1897, **21**, 664. See also H. Nidenführ, Belg. P. 182063, 1905.

3. Zts. ang. Chem. 1902, **15**, 242; abst. J. S. C. I. 1902, **21**, 475; Tech. Chem. Jahr. 1902, **25**, 73.

4. D. R. P. 140825; abst. Zts. ang. Chem. 1903, **16**, 379; Chem. Centr. 1903, **74**, I, 1008; Jahr. Chem. 1903, **56**, 342; Chem. Ztg. 1903, **27**, 392; Wag. Jahr. 1903, **49**, I, 266; Chem. Zts. 1903, **2**, 713; 1904, **3**, 12. See F. Lüty, Zts. ang. Chem. 1905, **18**, 1255; abst. Eng. Min. J. 1905, 634. E. P. 1066, 1904; abst. J. S. C. I. 1904, **23**, 714; Chem. Ztg. 1905, **29**, 571.

5. E. P. 7127, 1897; Belg. P. 126944, 1897; abst. J. S. C. I. 1897, **16**, 537.

6. E. P. 28743, 1913; abst. J. S. C. I. 1915, **34**, 226; Zts. ang. Chem. 1916, **29**, I, 115; Chem. Ztg. Rep. 1915, **39**, 297; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110.

7. E. P. 28550, 1913; abst. J. S. C. I. 1915, **34**, 904; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110.

8. F. P. 449035; abst. Mon. Sci. 1914, **81**, 4.

9. D. R. P. 184959, 1904; abst. C. A. 1907, **1**, 3073.

10. U. S. P. 699011; abst. Chem. Zts. 1903, **2**, 8; Mon. Sci. 1902, **58**, 183.

11. D. R. P. 253493; abst. C. A. 1913, **7**, 687; Zts. ang. Chem. 1912, **25**, 2608; Chem. Zentr. 1912, **83**, II, 1953; Chem. Ztg. Rep. 1912, **36**, 648; Wag. Jahr. 1912, **58**, I, 376; Zts. Schiess. Spreng. 1913, **8**, 13.

12. E. P. 6617, 1914; abst. J. S. C. I. 1914, **33**, 830.

G. Schliebs,¹ H. Schmidl,² T. Meyer,³ W. P. Salessky,⁴ A. B. Foster,⁵ W. Fulda,⁶ L. A. Thiele,⁷ U. Wedge,⁸ J. Potut,⁹ W. H. Wagge-man,¹⁰ A. M. Fairlie,¹¹ O. Niederführ,¹² E. Hartmann,¹³ L. Ménard-Dez,¹⁴ H. Petersen.¹⁵

A discussion between G. Lunge and M. Neumann,¹⁶ on the reaction in the Glover tower, seems to have resulted in favor of the former.

This tower is usually erected side by side with the Gay-Lussac tower, so that their tops are accessible by a common stair. The supply of nitrous vitriol and chamber acid is regulated by the strength and nitrosity of the Gay-Lussac acid, since the main function of the Glover tower is the complete denitration of this acid. The final acid may be concentrated to 152° Tw. with good

1. U. S. P. 1151294, 1915; abst. J. S. C. I. 1915, **34**, 1009; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111.
2. Zts. ang. Chem. 1908, **21**, 249; abst. J. S. C. I. 1908, **27**, 223.
3. Zts. ang. Chem. 1909, **22**, 1841; abst. C. A. 1910, **4**, 649.
4. E. P. 20131, 1910; abst. C. A. 1911, **5**, 3135; J. S. C. I. 1911, **30**, 489; Chem. Ztg. Rep. 1912, **36**, 43.
5. U. S. P. 1277896, 1918; abst. J. S. C. I. 1918, **37**, 732-A; Mon. Sci. 1919, **86**, 26.
6. U. S. P. 1048953; abst. C. A. 1913, **7**, 686; Mon. Sci. 1913, **79**, 99.
7. U. S. P. 1267012, 1918; abst. J. S. C. I. 1918, **37**, 500-A.
8. U. S. P. 1104590, 1914; abst. J. S. C. I. 1914, **33**, 864; C. A. 1914, **8**, 3102; Chem. Ztg. Rep. 1915, **39**, 114; Mon. Sci. 1914, **81**, 178.
9. E. P. 7710, 1901; abst. J. S. C. I. 1902, **21**, 706.
10. E. P. 101408, 1916; abst. C. A. 1917, **11**, 88; J. S. C. I. 1917, **36**, 647.
11. U. S. P. 1185029; abst. C. A. 1916, **10**, 1916; J. S. C. I. 1916, **35**, 736; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 177.
12. U. S. P. 1205723; abst. C. A. 1917, **11**, 191; J. S. C. I. 1917, **36**, 82; Mon. Sci. 1917, **84**, 51.
13. D. R. P. 206877, 1906; abst. C. A. 1909, **3**, 1919; Chem. Zentr. 1909, **80**, I, 1126; Chem. Ztg. Rep. 1909, **33**, 137; Wag. Jahr. 1909, **55**, I, 338; Zts. Schiess. Spreng. 1909, **4**, 108.
14. D. R. P. 284636, 1912; abst. J. S. C. I. 1915, **34**, 1090; Zts. ang. Chem. 1915, **28**, 364; Chem. Zentr. 1915, **86**, II, 168; Chem. Ztg. Rep. 1915, **39**, 244; Mon. Sci. 1917, **84**, 77.
15. F. P. 354073; abst. J. S. C. I. 1905, **24**, 1066; Mon. Sci. 1906, **65**, 108; Chem. Zts. 1906, **5**, 121.
16. Zts. ang. Chem. 1907, **20**, 1102. E. P. 27738, 1907; abst. J. S. C. I. 1908, **27**, 981. D. R. P. 208028; abst. Zts. ang. Chem. 1909, **22**, 748; Chem. Zentr. 1909, **80**, I, 1279; Jahr. Chem. 1909, **62**, I, 487; Chem. Ztg. Rep. 1909, **33**, 186; Wag. Jahr. 1909, **55**, I, 337; Zts. Schiess. Spreng. 1909, **4**, 216. D. R. P. 219829, 225196, 225197; abst. Wag. Jahr. 1910, **56**, I, 408, 409; C. A. 1911, **5**, 575, 3127; Zts. ang. Chem. 1910, **23**, 1052, 2098, 2099; Chem. Zentr. 1910, **81**, I, 1074; II, 931; Jahr. Chem. 1910, **63**, I, 523; Chem. Ztg. Rep. 1910, **34**, 151, 467, 481; Mon. Sci. 1913, **79**, 159; 1914, **81**, 87.
17. G. Lunge, Zts. ang. Chem. 1906, **19**, 1931; abst. C. A. 1907, **1**, 343. Zts. ang. Chem. 1907, **20**, 267; abst. C. A. 1907, **1**, 1046. M. Neumann, Zts. ang. Chem. 1906, **19**, 1702; abst. C. A. 1907, **1**, 87. Zts. ang. Chem. 1907, **20**, 264; abst. C. A. 1907, **1**, 1046. Chem. Ztg. 1906, **30**, 1078; abst. C. A. 1907, **1**, 227.

working. If the chamber acid tests 123° Tw. = 70% H_2SO_4 , 117 parts of this acid correspond with 100 parts of acid of 152° Tw. = 81.7% H_2SO_4 , or 100 volumes of the latter are equivalent to 128 volumes of 123° acid. These proportions would be run into the Glover tower. The resulting acid would test 136° Tw., and can be fully denitrated in passing down the tower.

The temperature of the acid issuing from the Glover tower is usually between 120° and 130° , but may reach 140° or even 150° without detrimental results. The retention of flue dust by the tower leads to contamination of the acid with iron, which may give trouble in the subsequent concentration; alumina may also be dissolved from the lining. Owing to contamination, the gravity of the acid does not correspond with its titration.

Recovery of Nitrogen Compounds. The methods in use before the introduction of the Glover tower for the denitration of nitrous vitriol are now merely of historical interest. Large Woulfe's bottles were in some cases used for effecting the denitration. A description of the older processes is given by F. Bode.¹ Gay-Lussac employed a small lead tower packed with coke, down which the nitrous vitriol trickled, and was met by a jet of steam. Burner gas was at the same time passed through the tower. In other cases the nitrous vitriol was run into small boxes with water, into which steam passed. Columns, lined with acid-resisting bricks, through which steam was passed, were also employed. Such denitrating towers are in use at present for recovering the nitrogen oxides from sulfuric acid used in the manufacture of explosives, but are not applied in sulfuric acid work. With suitable regulation of the steam supply, the denitration can be very efficiently conducted, since nitrous vitriol loses practically the whole of its nitrogen compounds when diluted within very narrow limits of concentration.

A detailed account of the function of the Glover tower in denitrating acid has been given by E. Sorel.² According to his researches the lower hottest layers of acid of 62° Bé. leaving the tower are unable to dissolve nitrogen oxides partly on account of the high temperature and also on account of the dilution with inert gas. The acid is thus practically completely denitrated.

1. Dingl. Poly. 1877, **223**, 90, 185, 290, 393, 504, 621; **224**, 298; **225**, 180.

2. "La Grande Industrie chimique minerale," Paris, 1902.

In the upper layers the acid is cooler and weaker, say 55° Bé., and absorbs water vapor given off by the lower layers. When reduced to 54° Bé. it can retain only 2.216 mgm. N_2O_3 per liter at 65° . Denitration of the nitrous vitriol fed in with the weak chamber acid therefore occurs rapidly in this region. This mode of operation corresponds with the old method of operating the Glover tower.

In the modern method of intensive working, a considerable amount of nitrous vitriol is run down the tower, for two purposes: (i) to cool the gases, (ii) to increase the stock of circulating nitrogen oxides. In this case the acid will leave the base of the tower almost completely denitrated, as before, because the conditions there remain unchanged, but the zone of denitrification will extend more into the upper part of the tower, since the quantity and concentration of the acid to be denitrated have both increased, while the temperature has been lowered by the large volume of cold nitrous vitriol.

Assume the stock of nitrous vitriol in circulation has been increased and the air supply reduced to the minimum, say 4% of oxygen in the exit gas from the chambers. Let the circulating niter, in the form of nitrogen oxides in the gases and dissolved in the nitrous vitriol be 24% of the sulfur burnt as 50% pyrites. One liter of the gas at S. T. P. will then be leaving the Glover tower with 14 mgm. N_2O_3 . Under these conditions, according to Sorel, 56.5° Bé. acid, i. e., acid somewhat diluted by aqueous vapor from the lower part of the Glover tower, can still contain 14.5 mgm. N_2O_3 per liter. The zone of denitrification will therefore not begin at this point, but lower down in the tower where the temperature is higher. In these regions, however, the acid will become more concentrated, and must be raised to a still higher temperature before it will release all the nitrous vapors. Thus, 58° Bé. acid at 90° can still retain 4.64 mgm. N_2O_3 per liter in an atmosphere containing 2.7 mgm. N_2O_3 per liter, and in this second zone the tension of the gas will be 8.3 mgm. N_2O_3 per liter. There will therefore be successive zones of denitrification in the Glover tower, each at more or less fixed temperatures in steady working, and through which acid of more or less uniform concentration is passing. The temperature and concentration of the acid increases in passing downwards, and these factors act

in opposition in the denitrification of the acid. The effect of temperature prevails at the base of the tower, and practically all the nitrous vitriol is decomposed.

It follows from the above that the height of the Glover tower is fixed by the zones of denitrification, i. e., by the temperature of the burner gas, and the volume of acid run through the tower. Since these are relatively more or less the same in different works, it is clear that increase of capacity of the Glover tower can be made only in its diameter, and retaining a constant height.

In such intensive working, i. e., high niter circulation, there will be a high concentration of nitrogen oxides in the Glover tower, together with an intimate contact between acid and burner gas. The proportion of acid formed in the tower may then, as has been stated, rise to 25% of the total produced.

Another effect of this large production of acid is also to fix a considerable proportion of the steam driven out in the lower parts of the tower, with the result that there is very little dilution of the Gay-Lussac acid in the upper layers of the tower.

The tables given by Sorel for the tensions of N_2O_3 in nitrous vitriols of different strengths have been extensively used. J. Partington finds that the numbers of Sorel are in general agreement with his results, although they are probably not sufficiently accurate to enable very reliable conclusions to be drawn. He finds that the zone of denitrification at a given temperature is very sharply defined, a small change in the gravity of the acid leading to almost complete denitrification. The efficiency of column denitrifiers supplied with steam can therefore, without undue dilution of the acid, attain well over 95%.

J. Gessert¹ has proposed to absorb the nitrous gases in water. To assist the absorption in the Gay-Lussac tower, F. Benker and H. Lasne² add sulfur dioxide to the gases passing to the Gay-Lussac tower, to reduce nitrogen peroxide to trioxide. A. Izidore and M. Biscons³ use an apparatus composed of lead baffle plates, over which sulfuric acid flows, to absorb nitrous gases instead of,

1. E. P. 2077, 1869.

2. E. P. 4522, 1880; abst. Chem. Ind. 1882, 5, 138. E. P. 3540, 1880; abst. J. A. C. S. 1882, 4, 45.

3. E. P. 19007, 1898; abst. J. S. C. I. 1899, 18, 831. Belg. P. 137962, 1898. Swiss P. 17888, 1898.

or in addition to, a Gay-Lussac tower. O. Eliel¹ uses a denitrating and concentrating tower provided with a number of independent filled sections, above which a valved flue connects with the burners, union with the chambers being made below the sections. The tower is closed at the top, and a spray nozzle arranged in the entering flue for the sulfurous gases. A down draft is produced in the tower by suitable means. I. Hechenbleikner and the Southern Electro-Chemical Co., N. Y.,² spray nitrous vitriol into a current of steam, introducing oxygen into the resulting gases to produce nitric acid fumes, which are subsequently condensed. W. Salesky³ denitrates with air in the absence of sulfur dioxide, obtaining nitrogen oxides, which are then mixed with sufficient air to convert them into NO₂. The utility of this invention is obscure. H. Welch⁴ precipitates nitrogen oxides, nitrosulfonic acid and sulfuric acid mist from the exit gases by an electric discharge. E. Kauffmann⁵ causes a mixture of nitrogen oxides, sulfur dioxide, steam and atomized water to react in a closed vessel at 150°–200°. W. Fulda⁶ regenerates nitric acid in a series of chambers comprizing 20, 30 and 50% of the total space, and subjects the nitrogen oxides in the chambers to acid of sp. gr. 1.21–1.26, 1.07–1.21 and 1.00–1.10, respectively. Recovery apparatus for nitrogen oxides has been described by A. Lynn,⁷ F. B. Hacker and P. S. Gilchrist,⁸ E. J. Barbier,⁹ the Société Le Nitrogène,¹⁰ the

1. U. S. P. 725427, 1903; abst. J. S. C. I. 1903, **22**, 627; J. A. C. S. 1903, **25R**, 522.

2. U. S. P. 1264512, 1918; abst. C. A. 1918, **12**, 1690; J. S. C. I. 1918, **37**, 414-A.

3. E. P. 20131, 1910; abst. C. A. 1911, **5**, 3135; J. S. C. I. 1911, **30**, 489; Chem. Ztg. Rep. 1912, **36**, 43. F. P. 419609, 1910; abst. C. A. 1912, **6**, 1967; Chem. Ztg. Rep. 1911, **35**, 129; Mon. Sci. 1913, **79**, 88. D. R. P. 232570, 1909; abst. C. A. 1911, **5**, 2709; Zts. ang. Chem. 1911, **24**, 717; Chem. Zentr. 1911, **82**, I, 1088; Chem. Ztg. Rep. 1911, **35**, 180; Wag. Jahr. 1911, **57**, I, 421. Aust. P. 50405, 1911. Swiss P. 52712, 1910.

4. U. S. P. 1284166; abst. C. A. 1919, **13**, 166; J. S. C. I. 1919, **38**, 73-A. E. P. 134015, 1918; abst. J. C. S. I. 1919, **38**, 946-A.

5. D. R. P. 226219, 1909; abst. C. A. 1911, **5**, 1326; Zts. ang. Chem. 1910, **23**, 2294; Chem. Zentr. 1910, **81**, II, 1254; Jahr. Chem. 1910, **63**, I, 624; Chem. Ztg. Rep. 1910, **34**, 527; Wag. Jahr. 1910, **56**, I, 413; Mon. Sci. 1914, **81**, 87.

6. U. S. P. 1048953; abst. C. A. 1913, **7**, 686; Mon. Sci. 1913, **79**, 99.

7. E. P. 11452, 1912; abst. C. A. 1913, **7**, 3657; J. S. C. I. 1912, **31**, 1167; Chem. Ztg. Rep. 1912, **36**, 556.

8. E. P. 15895, 1893; abst. J. S. C. I. 1893, **12**, 1032.

9. E. P. 14014, 1894; abst. J. S. C. I. 1895, **14**, 749.

10. F. P. 404071; abst. C. A. 1911, **5**, 1664; Chem. Ztg. Rep. 1910, **34**, 18; Mon. Sci. 1910, **73**, 160.

Soc. Anon. Ing. L. Vögel,¹ the Badische Co.,² and R. Lal Datta.³

Mechanical washers for the absorption of the nitrous gases leaving the last chamber have been proposed.⁴

Combined Chamber and Contact Process. N. Heinz and M. Chase⁵ proposed to combine the working of the chamber and contact processes by passing the burner gases through a dust flue, a Glover tower, and a Gay-Lussac tower. The residual gases were filtered, heated, and passed over some contact mass without special purification, beyond that involved in the preceding processes. W. Alcock and G. Davis⁶ operate in the inverse order. The burner gas is made in closed kilns with air dried with Glover acid, which after use is sent to the Gay-Lussac tower. The dry sulfur dioxide and air is then passed to an iron oxide contact mass, the sulfur trioxide absorbed in sulfuric acid, and the residual gas then passed to lead chambers for the conversion of the remaining sulfur dioxide.

W. Wilke⁷ has described a combination of the contact and chamber processes. The plant dealt with 24,000 lbs. fines and 36,000 lbs. lump ore daily, thirty-six burners being installed, each capable of handling 900 to 1,200 lbs. of ore daily, and four Herreshoff burners for fines. The burner gases were conducted into a flue situated above the flue of the lump burners and provided with a number of baffle walls to retain some of the dust. The gases of the lump and fine burners were united and conducted into an iron oxide contact shaft of the Mannheim type. In order to regulate the draft of the fines burners, a separate exhaust fan was installed to draw the gases from the burners and deliver them to the flue above the lump burners. A second exhaust fan in-

1. E. P. 6846, 1904; abst. J. S. C. I. 1904, **23**, 1088.

2. D. R. P. 238360; abst. C. A. 1912, **6**, 1063; Zts. ang. Chem. 1911, **24**, 2069; Chem. Zentr. 1911, **82**, II, 1077; Chem. Ztg. Rep. 1911, **35**, 529; Wag. Jahr. 1911, **57**, I, 468; Zts. Schiess. Spreng. 1911, **6**, 411.

3. India P. 2523, 1916.

4. *Alkali Insp. Rep.* 1915; Chem. Trade J. 1916, 284. See also N. Heinz and H. Petersen, D. R. P. 217723; abst. Wag. Jahr. 1910, **56**, I, 411. A. Teraud and P. Truchot, F. P. 425913, 1910, and additions thereto; abst. J. S. C. I. 1911, **30**, 1012, 1381; 1913, **32**, 600. H. and J. Wilson and A. French, E. P. 5239, 1878.

5. U. S. P. 875909, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 94; Mon. Sci. 1908, **69**, 51.

6. E. P. 16981, 1915; abst. C. A. 1917, **11**, 1526; J. S. C. I. 1917, **36**, 82.

7. Eight Intl. Cong. Appl. Chem. 1912, **2**, 249; Discussions, **27**, 32; abst. C. A. 1913, **7**, 869, 2455; J. S. C. I. 1912, **31**, 874. J. Ind. Eng. Chem. 1912, **4**, 840. Chem. Trade J. 1912, **51**, 294.

stalled between the oxide shaft and the Glover tower, takes the sulfurous gases after they had undergone conversion to the extent of 30% in the oxide shaft, and draws these gases to the chamber plant.

This combination gave excellent results, the capacity of the chamber plant being increased by at least 30%. The conversion of SO_2 into SO_3 in the oxide shaft averaged 30%. The acid produced in the Glover tower was water-white, and 95% of the arsenic oxide eliminated in the contact shaft. The total production in the chamber system could be concentrated to 60° Bé. or higher in the Glover tower. The oxide shaft retards the dust, acts as a heat accumulator and equalizer, enabling the operation to be carried out uniformly. The conversion in the oxide shaft leads to an economy in niter of 30%. Any type of chamber plant may have an oxide shaft installed between the burners and the Glover tower.¹

Various Processes for the Manufacture of Sulfuric Acid. In addition to the ordinary chamber process and modifications of it, numerous special processes have been proposed for the manufacture of sulfuric acid, not one of which, so far as is known, is in use at the present time.

H. Deacon² proposed to obtain acid from sulfides and chlorine. F. Stanes and G. Rogé³ utilize part of the heat given off in the combustion of sulfur for driving off sulfuric acid from acid sulfates. M. Hanahan⁴ burns sulfur or sulfurous material in the dust chamber. O. Wentzki⁵ employs a series of rotating cylinders in tandem arrangement, provided interiorly with ridges or grooves through which the reaction gases pass in countercurrent flow to the acid or nitrous vitriol. N. Pratt⁶ cools the gases in chambers or towers by external jackets containing a cooling medium. C. Meigs⁷ varies the density of the gases by alternate

1. F. Lütj and H. Niedenführ (Zts. ang. Chem. **15**, 242; abst. J. S. C. I. 1902, **21**, 475) discuss the relative advantages of the chamber and the contact processes.

2. E. P. 3098, 1868.

3. E. P. 29254, 1913; abst. J. S. C. I. 1915, **34**, 227; Mon. Sci. 1917, **84**, 73.

4. U. S. P. 1253238, 1918; abst. J. S. C. I. 1918, **37**, 148-A.

5. D. R. P. 230534, 1910; abst. C. A. 1911, **5**, 2707. D. R. P. 238960, 1909; abst. C. A. 1912, **6**, 1971.

6. U. S. P. 715142, 1902; abst. J. S. C. I. 1903, **22**, 93. E. P. 4856, 1895; abst. J. S. C. I. 1895, **14**, 806.

7. U. S. P. 1022493, 1912; abst. J. S. C. I. 1912, **31**, 686.

compression and expansion by means of a special baffle in the chamber. G. de Briailles¹ oxidizes sulfur dioxide electrolytically in a special cell. J. Fels² operates stirring devices inside the chambers. J. Pintsch, H. Strache and H. Hiller³ describe the oxidation of sulfuretted hydrogen to sulfuric acid in presence of ferrous salts. J. Mackenzie⁴ uses a series of long tunnels instead of chambers. H. Rabe⁵ describes modifications of the chambers to obtain better mixing. A. Düron details two independently operating reaction towers, in connection with Gay-Lussac and Glover towers.⁶ E. and T. Deplace⁷ describe a special type of lead chamber formed in the shape of a ring, with a sector cut out for the towers. The Pratt Process Co.⁸ return a portion or the whole of the partially spent gases through the system. F. Carmichael and F. Guillaume⁹ employ a series of independent vertical chambers, alternately empty and packed. W. Kee and U. Wedge¹⁰ expose the gases after leaving the Glover tower to electric discharges. G. and A. Davis¹¹ connect the different chambers by a large number of tubes of small diameter, which serve to mix and cool the gases. E. Barbier¹² describes a series of reaction towers heated at the base, so as to obtain concentrated acid. A. Fairley¹³ has detailed a means of control of chamber plants by well known methods of gas analysis. A. Zanner¹⁴ places concentrating pans in the flue of the Glover tower. The Societa Anon. Ing. L. Vogel¹⁵ describe iron cylinders, containing niter and sulfuric acid, heated by gases from the burners, for supplying the

1. F. P. 393665, 1907; abst. J. S. C. I. 1909, **28**, 138. Australian P. 13148, 1908.
2. D. R. P. 228696, 1909; abst. J. S. C. I. 1911, **30**, 85.
3. D. R. P. 283601; abst. Oest. Chem. Ztg. 1917, **20**, 14.
4. E. P. 19084, 1913; abst. C. A. 1915, **9**, 360.
5. D. R. P. 217561, 1909; abst. J. S. C. I. 1911, **30**, 1159. Zts. ang. Chem. 1910, **23**, 8.
6. F. P. 453733, 1913; abst. C. A. 1913, **7**, 3645; J. S. C. I. 1913, **32**, 790.
7. E. P. 5058, 1890; abst. J. S. C. I. 1891, **10**, 254.
8. E. P. 10757, 1899. Belg. P. 142809, 1899.
9. E. P. 15679, 1913; abst. J. S. C. I. 1914, **33**, 830. See also E. P. 9317, 1904. 22080, 1905.
10. U. S. P. 1220752, 1917; abst. J. S. C. I. 1917, **36**, 547.
11. E. P. 20012, 1904; abst. J. S. C. I. 1905, **24**, 925.
12. E. P. 12726, 1892; abst. J. S. C. I. 1893, **12**, 602.
13. U. S. P. 1205723, 1205724; abst. J. S. C. I. 1917, **36**, 82, 83, 196; C. A. 1917, **11**, 191. Chem. Trade J. Jan. 27, 1917.
14. U. S. P. 768108, 1904; abst. J. S. C. I. 1904, **23**, 900.
15. E. P. 6846, 1904; abst. J. S. C. I. 1904, **23**, 1088.

Gay-Lussac tower with an ample supply of nitrous vapors.

N. Heinz¹ uses towers with alternate free and packed spaces. N. Heinz² and H. Hegeler³ withdraw the gases from part of the system and pass them back to the Glover tower, to obtain more concentrated acid. Z. Littmann⁴ uses specially shaped chambers. J. Parent⁵ sprays nitrous vitriol into the chambers, or into small intermediate towers. O. Carlson and Hartmann & Benker⁶ describe a filter for gases. R. Cellarius⁶ removes sulfuric acid from gases by forcing the latter through two concentric perforated cylinders. Curtius & Co.⁷ introduce the gases at a lower temperature than usual into the first tower of a series. L. Santa⁸ describes an apparatus for regulating the density of sulfuric acid. J. McNab⁹ introduces nitrogen oxides from a denitrating column into the chambers to restore the latter when deficient in niter.¹⁰

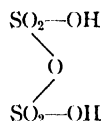
1. U. S. P. 728914, 1903; abst. J. S. C. I. 1903, **22**, 742. U. S. P. 1057149, 1913; abst. J. S. C. I. 1913, **32**, 424. N. Heinz and M. Chase, U. S. P. 875909. See also R. Heinz, D. R. P. 264640, 1911; abst. J. S. C. I. 1913, **32**, 1066.
2. U. S. P. 752677, 1904; abst. Chem. Zts. 1904, **3**, 516, 655; J. A. C. S. 1904, **26R**, 407; Mon. Sci. 1905, **63**, 7.
3. F. P. 462668, 1913.
4. F. P. 449035, 1911; abst. Mon. Sci. 1914, **81**, 4.
5. F. P. 372644, 1906. Belg. P. 196703, 1906; abst. Chem. Ztg. Rep. 1907, **31**, 324.
6. D. R. P. 166745; abst. Wag. Jahr. 1905, **51**, 395; Chem. Centr. 1906, **77**, I, 420. D. R. P. 183097; abst. C. A. 1907, **1**, 3072.
7. E. P. 28550, 1913; abst. J. S. C. I. 1915, **34**, 904.
8. E. P. 18015, 1913; abst. J. S. C. I. 1914, **33**, 485. F. P. 461041; abst. J. S. C. I. 1914, **33**, 199.
9. U. S. P. 325262, 325263, 1885.
10. Other proposed methods for the manufacture of sulfuric acid are: K. Auer, Swiss P. 74525, 1917. F. Benker and H. Lasne, E. P. 1957, 1881; abst. J. S. C. I. 1881, **1**, 189. Brante & Co., Swiss P. 13228, 1896. J. Carmichael and F. Guillaume, E. P. 15679, 1913; abst. J. S. C. I. 1914, **33**, 830. G. de Briailles, U. S. P. 928844. T. Dotterer, U. S. P. 270763, 1883. J. Eggleston, U. S. P. 908400, 1908; U. S. P. 1018040, 1912. L. Fauchaux, Second addition, May 10, 1902, to F. P. 307359; abst. J. S. C. I. 1903, **22**, 420. A. Gaillard, U. S. P. 909578, 1909. G. Hanisch, U. S. P. 477755, 1892. B. Hart and G. Bailey, J. S. C. I. 1903, **22**, 473; J. Soc. Dyers Col. 1903, **19**, 201. E. Hartmann and F. Benker, D. R. P. 282747, 1913; abst. C. A. 1915, **9**, 2437. E. Haworth, U. S. P. 268793, 1882. J. Herreshoff, U. S. P. 737233, 1903; abst. J. S. C. I. 1903, **22**, 1045. D. Jackson, U. S. P. 130432, 1872. W. Johnson, U. S. P. 825057, 1906. E. Labois, U. S. P. 233680, 1880. J. McNab, U. S. P. 798524, 1905. R. Moritz, U. S. P. 981103, 1911. A. Nibelius, U. S. P. 873070, 1907. A. O'Brien, U. S. P. 694024, 1902. H. Petersen, Zts. ang. Chem. 1907, **20**, 1101; abst. C. A. 1907, **1**, 2293. D. R. P. 258554, 1912; abst. J. S. C. I. 1913, **32**, 600. U. S. P. 904147. E. P. 27738, 1907; abst. J. S. C. I. 1908, **27**, 981. W. Quinn, U. S. P. 699011, 1902; abst. J. S. C. I. 1902, **21**, 772. J. Raschen, C. Imison and United Alkali Co., E. P. 30196, 1909. C. Robinson, U. S. P. 1018374, 1912. G. Schliebs, U. S. P. 1151294; abst. C. A. 1915, **9**, 2798. A. Sebillot,

G. Chrisp¹ discusses the possibilities of the manufacture of sulfuric acid from the sulfur contained in coal.

Pyrosulfuric Acid. The compound $2\text{SO}_3 \cdot \text{H}_2\text{O}$, or $\text{H}_2\text{S}_2\text{O}_7$, is a definite hydrate of sulfur trioxide, known as pyrosulfuric acid. It was formerly prepared in Bohemia by the dry distillation of ferric sulfate, and is sometimes called Nordhausen, or fuming sulfuric acid, since it evolves dense white fumes when exposed to air. The pure compound, which contains 89.89% SO_3 and 10.11% H_2O , is a transparent crystalline mass, melting at 35° , although fuming acid is a thick, oily liquid, hence it is now usually called oleum. It decomposes on heating, giving off fumes of SO_3 and leaving ordinary sulfuric acid.

Pyrosulfuric acid may be obtained by cooling ordinary liquid oleum, when the acid crystallizes out, or by adding the calculated amount of sulfur trioxide to cooled concentrated sulfuric acid, and cooling.

The formula of the acid is believed to be:



Pyrosulfuric acid forms salts, those of the alkali metals being

U. S. P. 230501, 1880. Cf. Belg. P. 138197, 1898. Soc. Anon., L. Vogel, etc., Aust. P. 21601, 1905. H. Sprengel, U. S. P. 150095, 1874. U. S. P. 357107, 1887. T. Terrell, U. S. P. 308289, 1884. H. Welch, U. S. P. 1285856; abst. C. A. 1919, **13**, 250. U. Wedge, U. S. P. 1106999. E. Barbier, E. P. 10450, 1892; abst. J. S. C. I. 1893, **12**, 44.

1. Gas J. 1919, **145**, 173; Gas World, 1919 (Coking and By-Products Sect.), **70**, No. 1802, 13; abst. C. A. 1919, **13**, 994. The Amer. Fertilizer, 1919, **50**, No. 4, 29; abst. J. I. E. C. 1919, **11**, 391. J. Hepworth, J. S. C. I. 1884, **3**, 158. A. McDougall, Belg. P. 142758, 1899. Norske Aktieselskab f. Elektrisk-Kemisk Industri, Norw. P. 24038. K. Quinan, E. P. 130712; abst. J. S. C. I. 1919, **38**, 717-A. H. Baker, U. S. P. 86200, 1869. W. and A. Elmore and H. Barrett, E. P. 15988, 1885; abst. J. S. C. I. 1887, **6**, 140. M. Devilaire, F. P. 423893, 1911. J. Darling, U. S. P. 541597, 1895. J. Hanson, E. P. 10818, 1887; abst. J. S. C. I. 1888, **7**, 626. J. Hall, T. Gibb and C. Gelstharp, E. P. 3143, 1871. A. Johnson, U. S. P. 621608, 1899. W. Johnson, U. S. P. 825057, 1906; abst. Mon. Sci. 1907, **67**, 12. R. and L. Labois, E. P. 4364, 1879. F. de Mare, Belg. P. 156619, 1901. M. Masson, F. P. 324859, 1902; abst. Mon. Sci. 1904, **61**, 43. A. Monnier, U. S. P. 17976, 1857; Re-502; Re-603, 1858. B. Nicholson and T. Palmer, E. P. 9777, 1889. L. Pratis and P. Marengo, E. P. 15509, 1897. A. Ramage, U. S. P. 984703, 1911; abst. Mon. Sci. 1911, **75**, 117. Taylor and Scott, E. P. 127047; abst. J. S. C. I. 1919, **38**, 446-A. H. Welch, E. P. 134015, 1918; abst. C. A. 1920, **14**, 803. J. Theiberg, E. P. 2789, 1907; abst. J. S. C. I. 1907, **26**, 1013. J. Behrens, D. R. P. 300036, 1915; abst. J. S. C. I. 1920, **39**, 20-A.

the best known. The use of sodium pyrosulfate for the production of oleum has been described. The pyrosulfates of the alkali metals are formed by heating the acid sulfates to dull redness:



At a bright red heat, they decompose, evolving sulfur trioxide and leaving the normal sulfate:



In solution in water the pyrosulfates gradually decompose into the acid sulfates, by taking up a molecule of water.

Persulfuric Acid and Persulfates. By the electrolysis of a concentrated solution of potassium bisulfate, crystals of potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$, separate at the anode. When these are dissolved in cold concentrated sulfuric acid, a solution of Caro's acid, H_2SO_5 , is formed. Perdisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$, and permonosulfuric acid, H_2SO_5 , have both been obtained in the pure state.¹

Persulfates are always prepared by electrolysis. The most soluble salt is ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Methods for the electrolytic preparation of persulfates have been disclosed by A. Pietzsch and G. Adolph,² E. Müller and O. Friedberger,³ the Verein Chem. Werke A. G.,⁴ the Farbenfabriken vorm. F. Bayer,⁵ and the Consortium f. Electrochem. Ind.⁶

The estimation of persulfates has been described by E. Müller and H. v. Ferber,⁷ C. Peters and S. Moody,⁸ G. Allard,⁹

1. C. Otin, Zts. Elektrochem. 1911, **17**, 919; abst. J. S. C. I. 1911, 1250.

2. U. S. P. 1059809; abst. J. S. C. I. 1913, **32**, 534. E. P. 23252, 1910; abst. J. S. C. I. 1911, **30**, 85. E. P. 23551, 1910; abst. J. S. C. I. 1911, **30**, 85.

3. See also E. P. 23157, 1910; abst. J. S. C. I. 1910, **29**, 1454. A. Pietzsch, Belg. P. 229401, 1910.

4. Zts. Elektrochem. 1902, **8**, 230; abst. J. S. C. I. 1902, **21**, 706.

5. D. R. P. 205067, 205068, 205069, 1907; abst. J. S. C. I. 1909, **28**, 96; Zts. ang. Chem. 1909, **22**, 209, 459, 460; Chem. Zentr. 1909, **80**, I, 232; Jahr. Chem. 1909, **62**, I, 490, 491; Chem. Ztg. Rep. 1909, **33**, 7; Wag. Jahr. 1908, **54**, I, 486; Mon. Sci. 1912, **77**, 53.

6. F. P. 470264, 1914; abst. J. S. C. I. 1915, **34**, 177. D. R. P. 271642, 1913; abst. J. S. C. I. 1914, **33**, 484; C. A. 1914, **8**, 2316; Zts. ang. Chem. 1914, **27**, 261; Chem. Zentr. 1914, **85**, I, 1234; Chem. Ztg. Rep. 1914, **38**, 177; Wag. Jahr. 1914, **60**, I, 421. E. P. 24931, 1913; abst. J. S. C. I. 1914, **33**, 749.

7. E. P. 23548, 1910; C. A. 1911, **5**, 3135; J. S. C. I. 1911, **30**, 421. F. P. 351613, 1905; abst. J. S. C. I. 1905, **24**, 896; Chem. Ztg. 1905, **29**, 843; Mon. Sci. 1906, **65**, 102; Chem. Zts. 1905, **4**, 303. Belg. P. 175690, 1904. G. Teichner and P. Askenasy, U. S. P. 880599, 1908; abst. J. S. C. I. 1908, **27**, 341; Mon. Sci. 1909, **71**, 32.

8. Zts. anal. Chem. 1913, **52**, 195, 299; abst. J. S. C. I. 1913, **32**, 286, 532.

9. Amer. J. Sci. 1901, (4), **12**, 367; abst. Chem. Centr. 1901, **72**, II, 1276; J. S. C. I. 1902, **21**, 140.

J. Pharm. Chim. 1901, **14**, 506; abst. J. S. C. I. 1902, **21**, 140.

C. Marie and L. Bunel,¹ D. Vitali,² and R. Wolfenstein and A. Wolff.³

The chief use of the persulfates is in photography, as "reducers."⁴ They have been suggested as sources of hydrogen peroxide.⁵ The action of various reagents on persulfates, as halogen acids,⁶ metallic oxides,⁷ mercury,⁸ manganese salts,⁹ potassium cyanide and silver nitrate,¹⁰ and organic substances,¹¹ has been described.

Miscellaneous Methods for Sulfuric Acid Manufacture. In addition to the well known methods of manufacturing sulfuric acid from pyrites and sulfur by the chamber and contact processes, a large number of special methods have been described, none of which appears to have been in use to any great extent. Some of these may be useful in special circumstances, although it is doubtful if they could be used with success in competition with the established processes.

The preparation of sulfuric acid from copper smelter gases has already been referred to,¹² and is, of course, a feasible method. The manufacture of the acid from ordinary materials in special

1. Bull. Soc. Chim. 1903, **29**, 930; abst. J. S. C. I. 1903, **22**, 1208.
2. Boll. Chim. Farm. 1902, **42**, 273, 321; abst. Chem. Centr. 1902, **73**, II, 312; J. S. C. I. 1903, **22**, 1016.
3. Ber. 1908, **41**, 717; abst. J. S. C. I. 1908, **27**, 355.
4. H. Marshall, Brit. J. Phot. 1902, **49**, 309, 444, 445; abst. J. S. C. I. 1902, **21**, 723, 989.
5. Consortium für Elektrochem. Ind., D. R. P. 199958, 1905; abst. J. S. C. I. 1908, **27**, 856.
6. E. Wedekind, Bull. Soc. Chim. 1902, **27**, 712; abst. J. S. C. I. 1902, **21**, 1074. See also N. Caro's reagent; abst. J. S. C. I. 1900, **19**, 172, 278, 777; 1901, **20**, 578. G. Teichner, U. S. P. 981900, 1911; abst. C. A. 1911, **5**, 1025; Chem. Ztg. Rep. 1911, **35**, 302; Mon. Sci. 1911, **75**, 117.
7. A. Seyewetz and P. Trawitz, Compt. rend. 1903, **137**, 130; abst. J. S. C. I. 1903, **22**, 906.
8. N. Tarugi, Gaz. chim. ital. 1903, **33**, 127; abst. Chem. Centr. 1903, **74**, I, 1116; J. S. C. I. 1903, **22**, 740.
9. M. Dittrich and C. Hassel, Ber. 1902, **35**, 3266; abst. J. S. C. I. 1902, **21**, 1414.
10. N. Tarugi, Gaz. chim. ital. 1902, **32**, 383; abst. Chem. Centr. 1903, **74**, I, 616; J. S. C. I. 1903, **22**, 493.
11. R. Datta and J. Sen, J. A. C. S. 1917, **39**, 747; abst. J. S. C. I. 1917, **36**, 567. See also M. Mugdan, Zts. Elektrochem. 1903, **9**, 719; abst. J. S. C. I. 1903, **22**, 1044. H. Armstrong and T. Lowry, Proc. Roy. Soc. 1902, **70**, 94; abst. J. S. C. I. 1902, **21**, 913. M. Levi, E. Migliorini and G. Ercolini, Gaz. chim. ital. 1908, **38**, I, 583; abst. J. S. C. I. 1908, **27**, 979. T. Price, Ber. 1902, **35**, 291; abst. J. S. C. I. 1902, **21**, 343.
12. E. Larison, Eng. Min. J. 1916, **162**, 1121; abst. J. S. C. I. 1917, **36**, 133.

apparatus has been described by C. Pâsques,¹ A. Burkhardt,² G. de Briailles,³ D. Peniakoff,⁴ P. Babatz,⁵ E. Thomson and W. Greene,⁶ P. Deerig,⁷ A. Sebillot,⁸ J. Chaffning,⁹ and others.

L. Jumau¹⁰ treats a solution of a copper salt under pressure with sulfur dioxide, obtaining a solution which is gradually heated, copper being precipitated and a solution of sulfuric acid obtained. A solution of ammonium sulfite may be used instead of sulfurous acid. F. Perry¹¹ acts on a solution of copper sulfate with hydrogen sulfide. The precipitated copper sulfide is converted completely into sulfate by calcination, a sufficient quantity of sulfuric acid being added to convert the copper oxide formed into sulfate. The invention is said to be particularly applicable to the removal of hydrogen sulfide from Mond and similar gases, the acid produced being used to extract the ammonia present in the gases. H. Roessler¹² passes a mixture of hot air with sulfurous acid, or sulfuric acid vapor, by a steam injector, through a perforated nozzle into an oxidizing liquid, which may consist of sulfuric acid with some nitric acid, or of copper sulfate or chloride solution, or a solution of ferrous sulfate or other metallic salts. Sulfurous acid is supposed to be converted into sulfuric acid, and if copper is present, copper sulfate obtained.

1. F. P. 441813, 1912; abst. J. S. C. I. 1912, **31**, 921. Belg. P. 254545, 1913.
2. F. P. 452682, 1912; abst. J. S. C. I. 1913, **32**, 608. Belg. P. 252160, 253126, 1913. D. R. P. 259576; abst. C. A. 1913, **7**, 3205; Zts. ang. Chem. 1913, **26**, 348; Chem. Zentr. 1913, **84**, I, 1903; Chem. Ztg. Rep. 1913, **37**, 300; Wag. Jahr. 1913, **59**, I, 374. D. R. P. 264921, 1912; abst. J. S. C. I. 1913, **32**, 1066; C. A. 1914, **8**, 220; Zts. ang. Chem. 1913, **26**, 632; Chem. Zentr. 1913, **84**, II, 1438; Chem. Ztg. Rep. 1913, **37**, 570; Wag. Jahr. 1913, **59**, I, 375; Zts. Schiess. Spreng. 1913, **8**, 416.
3. E. P. 22434, 1908; abst. C. A. 1910, **4**, 1530; J. S. C. I. 1909, **28**, 1199.
4. E. P. 21476, 1912; abst. C. A. 1914, **8**, 995; J. S. C. I. 1913, **32**, 424; Chem. Ztg. Rep. 1914, **38**, 128.
5. E. P. 1216, 1900; abst. J. S. C. I. 1900, **19**, 1110.
6. U. S. P. 143202, 1873.
7. U. S. P. 850820; abst. C. A. 1907, **1**, 1789; Chem. Ztg. Rep. 1907, **31**, 242; Mon. Sci. 1907, **67**, 153.
8. E. P. 2192, 1909; abst. C. A. 1910, **4**, 817; J. S. C. I. 1909, **28**, 1197.
9. F. P. 416988, 1910; abst. C. A. 1911, **5**, 2971; Mon. Sci. 1913, **79**, 83. Cf. D. Contaret, U. S. P. 11050, 1854.
10. E. P. 703, 1907; abst. J. S. C. I. 1907, **26**, 1241. See also E. P. 530, 1907; abst. J. S. C. I. 1907, **26**, 1204.
11. E. P. 20063, 1911; abst. C. A. 1913, **7**, 872; J. S. C. I. 1912, **31**, 534; Chem. Ztg. Rep. 1912, **36**, 481.
12. E. P. 5621, 1881. Dingl. Poly. 1881, **242**, 278; abst. Chem. Tech. Rep. 1881, **20**, II, 121.

J. Pintsch, H. Strache and H. Hiller¹ convert hydrogen sulfide contained in gases obtained by destructive distillation, into sulfuric acid. They claim that the conversion takes place in presence of solutions of ferric sulfate containing excess of sulfuric acid, with heat. The ferrous sulfate formed is to be regenerated alternately or simultaneously by air or oxygen. Under these conditions, oxidation to sulfuric acid without separation of sulfur is said to occur. The acid obtained contains iron and can be used as such or for combination with ammonia. In the latter case, after neutralization, any remaining ferrous sulfide may be separated and returned to the original oxidizing solution.

The preparation of sulfuric acid from sulfates has already been described. J. Auzies² calcines a mixture of gypsum and ferric oxide, whereby ferric sulfate and lime are formed: $3\text{CaSO}_4 + \text{Fe}_2\text{O}_3 = \text{Fe}_2(\text{SO}_4)_3 + 3\text{CaO}$. At a temperature above 800° the ferric sulfate decomposes into sulfur dioxide, oxygen and a residue of ferric oxide: $\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 3\text{O}$. The gases are then passed over manganese, or tungsten oxides, molybdic anhydride, or thoria, heated at first to above 200° . The first calcination may be carried out with a mixture of 408 parts calcined gypsum and 148 parts iron oxide at a temperature between 800° and 1500° . The action of ultraviolet light is stated to favor the union of the sulfur dioxide and oxygen. H. Frey³ describes experiments in which mixtures of gypsum and sand are calcined. The presence of small amounts of ferric oxide assists the decomposition, but addition of 0.5% ferric oxide does not appear to accelerate the decomposition beyond a certain point. L. Bassett⁴ heats a mixture of clay and a material containing calcium sulfate to a temperature sufficient to produce cement and gases containing sulfur dioxide. The latter, mixed with air, are passed over a contact material comprizing natural hydrated iron oxide

1. D. R. P. 283601, 1914; abst. C. A. 1915, **9**, 2442; Zts. ang. Chem. 1915, **28**, 311; Chem. Zentr. 1915, **86**, I, 1350; Chem. Ztg. Rep. 1915, **39**, 159.

2. F. P. 420675, 1910; abst. C. A. 1912, **6**, 1968; Chem. Ztg. Rep. 1911, **35**, 80; Mon. Sci. 1913, **79**, 80. See also Akt. Ges. Dynamit Nobel, D. R. P. 299035, 1910; abst. J. S. C. I. 1920, **39**, 64-A. Badische Anilin u. Sodafabrik, D. R. P. 298491, 1916; abst. J. S. C. I. 1920, **39**, 63-A.

3. Zts. ang. Chem. 1909, **22**, 2375; abst. C. A. 1911, **5**, 648. See also Chem. Fabrik Rhenania, D. R. P. 300716, 300763, 1916; abst. J. S. C. I. 1920, **39**, 109-A.

4. U. S. P. 1197331, 1916; abst. J. S. C. I. 1916, **35**, 1058. E. P. 124842, 1917; abst. C. A. 1919, **13**, 1747.

mixed with gypsum. The sulfur trioxide is removed, and the unconverted SO_2 absorbed in a calcareous material suitable for use in the production of cement. The German Government is stated¹ to have worked out a process for the production of sulfuric acid from gypsum and kieserite at a price not exceeding that from imported foreign pyrites. The cost of the necessary plant is stated to be \$700,000. The hope was expressed that the scheme would lead to the complete independence of Germany from foreign supplies in times of peace. C. Clemm² describes the treatment of kieserite, by calcining it in the presence of steam. The material is first powdered, washed free from chlorides, and compressed into balls. The vapors of sulfuric acid may be used in the treatment of poor ores. The sulfates may also be calcined with charcoal, and the sulfides decomposed to produce hydrogen sulfide, which is treated in the usual way. T. Terrel³ describes the calcination of a mixture of sulfur and iron sulfate, the gases being led into ordinary chambers.

W. Landis⁴ treats sulfur dioxide with excess of a gaseous mixture containing more than 6% of nitrous gases, produced by the oxidation of a mixture of ammonia and air.

The preparation of sulfuric acid by calcining aluminous schist or alum shale in closed retorts, is disclosed by J. Wilson.⁵ The preparation of sulfuric acid from sodium sulfate and bisulfate is described by F. Benker.⁶ Soc. Dior Fils⁷ calcine sulfates or bisulfates of natural or industrial origin (e. g., glauberite, alunite, etc.) with alumina, if the latter is not already contained in the material. The alumina may be added in the forms of powdered⁸ beauxite or aluminium sulfate. The operation is carried out in muffle furnaces, and the alkaline aluminate afterwards treated with carbon dioxide to produce alumina and alkaline carbonates.

The manufacture of sulfuric acid from waste products has been attempted. The utilization of smelter smoke as a source of sulfuric acid has been successful at the Ducktown Sulfur,

1. Chem. Trade J. Nov. 27, 1915; abst. J. S. C. I. 1915, **34**, 1205; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110.

2. E. P. 1776, 1863.

3. E. P. 5930, 1884; abst. Wag. Jahr. 1884, **30**, 276; 1885, **31**, 310.

4. U. S. P. 1173524, 1916; abst. J. S. C. I. 1916, **35**, 468.

5. E. P. 1522, 1800.

6. Aust. P. 29478, 1907.

7. F. P. 417816, 1909, and addition 13518, 1911, thereto; abst. C. A. 1912, **6**, 1966; Chem. Ztg. Rep. 1911, **35**, 321; Mon. Sci. 1913, **79**, 85.

Copper and Iron Co., Ducktown, Tenn.¹ The blast furnace gases after leaving the furnace dust chamber pass up a cylindrical tower through a kite-shaped flue to a special dust catcher at a higher level, the latter regulating the temperature of the gases delivered to the Glover tower, as well as eliminating zinc and other light dusts. From the dust catcher a brick flue runs the full length of the building with separate off-takes to each Glover tower. In each off-take is placed the niter pots, and an auxiliary set of pots provided in the dust-catcher in case of emergency. The dust-free gases then pass through two Glover towers; through which the gases are led to the top. They are then led downwards again to the base of a special tower, from the top of which they pass through two lead flues to the chambers. Upwards of 40% of SO₂ is converted into sulfuric acid in the towers. The chamber acid is concentrated in cast iron pans. The capacity of the plant is 160 tons 60° Bé. acid per day. The gases are passed through the chambers by four powerful fans of hard lead (10Sb + 90Pb). After the chambers are six Gay-Lussac towers, where nitrogen compounds are recovered. The acid discharged from the base of the Glover towers is clear and pure. The furnaces smelt pyrrhotite ore six days a week, the seventh day being devoted to the concentration of low-grade mattes produced during the ore-smelting period. The ore varies almost daily from 14%–19% S, and averages about 16%. The low grade matte averages about 25% S.

The manufacture of sulfuric acid from the gases from smelting pyrites has been discussed by F. Falding and J. Channing.² The vital points are stated to be: (1) The use of coke in excess of a certain percentage on the sulfur content of the charge. (2) The furnace from the tuyères up to the point where the gases are taken to the acid plant must be so designed that a controlled quantity of air in excess of that required in the matte-smelting process can be admitted at the tuyères, or between the tuyères and the top of the furnace, burden, or other suitable points. All admission of false air must be avoided as far as possible. The

1. W. Freeland and C. Renwick, *Eng. Min. J.* **89**, 1116; *abst. C. A.* 1910, **4**, 1897.

2. *Eng. Min. J.* **90**, 555; *abst. C. A.* 1910, **4**, 2981. D. R. P. 241509, 1909; *abst. C. A.* 1912, **6**, 2151; *Zts. ang. Chem.* 1912, **25**, 137; *Chem. Zentr.* 1912, **83**, I, 171; *Chem. Ztg. Rep.* 1912, **36**, 8; *Wag. Jahr.* 1911, **57**, I, 418; *Zts. Schiess. Spreng.* 1912, **7**, 78.

gases from more than one smelting furnace should be combined so as to ensure continuity of working of the acid plant.

The recovery of sulfuric acid from oil-refining residues has been described. R. C. Moffat and A. McLaren¹ run off the tarry mixture containing the acid from below the oil, and agitate with hot water. Tar separates, and the liquid portion is drawn off from below into a shallow iron box or lead-lined tank. The agitation of the tar with water is repeated. The acid is evaporated in a tank, any tar separating being skimmed off. A loose lead hood is placed over the tank in the later stages of the evaporation, the cooled acid then agitated with water, when empyreumatic matter separates. The acid is filtered through strong canvas stretched over the frames, the surface being frequently skimmed, the final concentration being performed in glass stills. A similar process has been described by F. Barrow,² who treats the residues with steam.

Sulfuric acid is recovered from the refuse "pickle" of tinplate works by allowing it to evaporate, and separating the crystals of ferrous sulfate.³ The mother liquor is further concentrated, and may be used again as pickle. The iron sulfate is distilled in retorts for the production of sulfuric acid. This is similar to the method of E. and C. Madge.⁴ A process of recovery from picric acid liquors has been evolved by C. Lowe,⁵ and the purification of waste acid⁶ detailed by E. Natho.⁷

Sulfuric Acid from Sulfates. In addition to the methods

1. E. P. 2200, 1871. See also L. Chandor, U. S. P. 42985, 1864.
2. E. P. 793, 1870.
3. W. Pughsley, E. P. 1538, 1864.
4. E. P. 3217, 1867.
5. E. P. 425, 1874.
6. D. R. P. 262466, 1912; abst. J. S. C. I. 1913, **32**, 826; C. A. 1913, **7**, 3534; Zts. ang. Chem. 1913, **26**, 477; Chem. Zentr. 1913, **84**, II, 552; Chem. Ztg. Rep. 1913, **37**, 438; Wag. Jahr. 1913, **59**, I, 381.
7. Still other methods of obtaining sulfuric acid and sulfur trioxide etc., are described by: H. Burburg, Belg. P. 228960, 1910. K. Burkheiser, E. P. 17359, 1910. G. Baldo, E. P. 5098, 1896. Chem. Fabrik Griesheim-Elektron, E. P. 20401, 1909; abst. C. A. 1914, **8**, 2418. F. P. 406641, 1909. M. Christie, E. P. 15817, 1910. T. Clarke and E. Smith, E. P. 4650, 1878. Erste Oesterr. Sodafabrik, E. P. 20171, 1908. G. Evans, E. P. 11338, 1907; abst. C. A. 1909, **3**, 231. J. Eastwick, E. P. 19369, 1908. G. Evans, E. P. 11338, 1907. W. Garroway, E. P. 1755, 1903. N. Helouis, E. P. 2080, 1881. J. Hargreaves and T. Bird, E. P. 18173, 1893. J. Hargreaves and T. Robinson, E. P. 1920, 1871. J. Hammond, E. P. 2376, 1878. C. Irvine and R. Slater, E. P. 3725, 1883. L. Juma, E. P. 530, 1907. A. French, Can. P. 145244, 1913; abst. C. A. 1913, **7**, 1269. P. Farup,

described in the preceding section for the manufacture of sulfuric acid from sulfates, a number of other processes have been proposed. O. Zahn,¹ C. Uebel² and U. Benker³ utilize sodium bisulfate (e. g., niter-cake, see p. 786). M. Prud'homme⁴ heats sulfates in the electric furnace with or without silica, alumina or iron oxide.

Some proposals for the utilization of gypsum or anhydrite have also been put forth. The enormous deposits of these minerals, which are of very little value as such, have led to numerous proposals for their employment. Processes of this nature have been described by R. Tilghman,⁵ Cary-Mantrand,⁶ O. Siemens,⁷ Kuenzi,⁸ O. Schott,⁹ Martin,¹⁰ N. Basset,¹¹ J. Shanks,¹² L. Margueritte,¹³ Fleck,¹⁴ H. Reinsch,¹⁵ F. Van Denbergh,¹⁶ H. Hilbert,¹⁷

U. S. P. 1219277, 1917; F. P. 454893, 1913; abst. J. S. C. I. 1913, **32**, 867; 1917, **36**, 457. C. Flodqvist, E. P. 4356, 1883. J. Knight, E. P. 5374, 1880. C. Meigs, U. S. P. 1120960; abst. C. A. 1915, **9**, 357. J. Mackenzie, E. P. 4770, 1913. G. Martin, E. P. 1540, 1869. D. Peniakoff, E. P. 14707, 1908. C. Polony, E. P. 1300, 1896. H. Rayner and W. Crookes, E. P. 2678, 1875. R. Schubardt, E. P. 16063, 1906. C. Westphal, E. P. 2823, 1882. C. Wigg, E. P. 9227, 1887. R. Ziegenberg, E. P. 14756, 1907. C. Weeks, U. S. P. 1048247. Clark, E. P. Appl. 13660, 1919; abst. J. S. C. I. 1919, **38**, 446-A. S. Paul, India P. 2847, 1916. E. Chaplin, U. S. P. 1325711, 1325712, 1919; abst. C. A. 1920, **14**, 453.

1. F. P. 389898; abst. Mon. Sci. 1909, **71**, 112. U. S. P. 921329; abst. Chem. Ztg. Rep. 1909, **33**, 339; Mon. Sci. 1909, **71**, 140.

2. D. R. P. 226110; abst. C. A. 1911, **5**, 1175; Zts. ang. Chem. 1910, **23**, 2294; Chem. Zentr. 1910, **81**, II, 1173; Jahr. Chem. 1910, **63**, 527; Chem. Ztg. Rep. 1910, **34**, 498; Wag. Jahr. 1910, **56**, I, 445; Mon. Sci. 1914, **81**, 87.

3. E. P. 1844, 1907; abst. J. S. C. I. 1908, **27**, 225. D. R. P. 204354; abst. Zts. ang. Chem. 1909, **22**, 178; Chem. Zentr. 1909, **80**, I, 113; Jahr. Chem. 1909, **62**, 914; Chem. Ztg. Rep. 1909, **33**, 13; Wag. Jahr. 1908, **54**, I, 376; Mon. Sci. 1912, **77**, 84. D. R. P. 204703; abst. Zts. ang. Chem. 1909, **22**, 169; Chem. Zentr. 1909, **80**, I, 413; Jahr. Chem. 1909, **62**, 489; Chem. Ztg. Rep. 1908, **21**, 662; Wag. Jahr. 1908, **54**, I, 376; Mon. Sci. 1912, **77**, 81; Chem. Zts. 1909, **8**, No. 1063. U. S. P. 899284. F. P. 381863; abst. Chem. Ztg. Rep. 1908, **32**, 276; Mon. Sci. 1909, **71**, 101.

4. F. P. 400030; abst. C. A. 1911, **5**, 574; Chem. Ztg. Rep. 1909, **33**, 445; Mon. Sci. 1910, **73**, 164.

5. E. P. 11555, 1847.

6. Barreswil and Girard, Diet. Chim. ind. **1**, 37.

7. Dingl. Poly. 1863, **169**, 207; abst. Wag. Jahr. 1863, **9**, 208.

8. Genie industriel, 1858, 280; abst. Wag. Jahr. 1858, **4**, 95. See also Archereau, Les Mondes, 1865, 319; abst. Dingl. Poly. 1865, **178**, 57; Poly. Centr. 1865, **31**, 1566; Wag. Jahr. 1865, **11**, 271.

9. Dingl. Poly. 1876, **221**, 442.

10. F. P. 96276; Bull. Soc. Chim. 1874, **21**, 47.

11. F. P. 331897.

12. E. P. 2161, 1854.

13. E. P. 2700, 1854.

14. Fabr. von chem. Prod. aus thier. Abfällen, 131.

15. Fürther Gewerbeztg, 1870, 46; Deut. Ind. Ztg. 1870, 235; abst.

H. Kenyon and I. Swindells,¹ E. Bong,² and others. The use of other sulfates has been described by J. Townsend,³ and also J. Capplemans.⁴

More promising processes are proposed by the following inventors: E. Natho,⁵ mixes gypsum and sand to a paste with a little water and heats in an autoclave for several hours at 600°–800°. P. Cantilena⁶ combines finely ground burnt gypsum and dried clay in such proportions that the ratio ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) to CaO is between 0.43 and 0.50. The mixture is made into a paste with water and moulded into blocks $20 \times 10 \times 10$ cm. After setting, the bricks are heated in furnaces in an abundant current of air and out of contact with fuel at a temperature of 1600°. The issuing gases are used for dehydrating gypsum. The residue is said to form a useful cement clinker. The Elektrizitätswerk Lonza⁷ heats a mixture of gypsum and quartz in an atmosphere enriched in oxygen to prevent dissociation of SO_3 . U. Cummings⁸ calcines gypsum with clay. R. Wedekind and Co.⁹ roast a mixture of gypsum, sand and pyrites. A. Bambach¹⁰ heats sulfates with an oxidizing flame produced by burning a mixture of gas and air.

The reduction of sulfates to sulfites, with subsequent recovery

Wag. Jahr. 1870, **16**, 167.

16. U. S. P. 642390; abst. Chem. Ztg. 1900, **24**, 148; Mon. Sci. 1900, **56**, 119.

17. D. R. P. 207761; abst. Zts. ang. Chem. 1909, **22**, 648; Chem. Zentr. 1909, **80**, I, 1207; Jahr. Chem. 1909, **62**, 490; Chem. Ztg. Rep. 1909, **33**, 186; Wag. Jahr. 1909, **55**, I, 346; Mon. Sci. 1912, **77**, 82. Belg. P. 207292, 1908. See also H. Trey, Zts. ang. Chem. 1909, **22**, 2375.

1. E. P. 1540, May 21, 1872.

2. E. P. 895, 1879.

3. E. P. 1703, 1879; abst. J. A. C. S. 1880, **2**, 193.

4. Belg. P. 149774, 1900. See also J. Darling, E. P. 12316, 1895; abst. J. S. C. I. 1895, **14**, 866. H. Deacon and F. Hurter, E. P. 15063, 1898. E. Daugnet, Belg. P. 145350, 1899.

5. D. R. P. 265835; abst. C. A. 1914, **8**, 409; Zts. ang. Chem. 1913, **26**, 675; Chem. Zentr. 1913, **84**, II, 1630; Chem. Ztg. Rep. 1913, **37**, 600; Wag. Jahr. 1913, **59**, I, 382.

6. Ital. P. Sept. 4, 1913; abst. C. A. 1914, **8**, 1331; Ind. Chim. **14**, 39.

7. Swiss P. 72627.

8. U. S. P. 342785; abst. Wag. Jahr. 1886, **32**, 264; J. A. C. S. 1886, **8**, 170. E. P. 7355, 7361, 1886; abst. J. Soc. Dyers Col. 1886, **2**, 110; Wag. Jahr. 1887, **33**, 496; 1888, **34**, 406.

9. D. R. P. 232784; abst. C. A. 1911, **5**, 2710; Zts. ang. Chem. 1911, **24**, 717; Chem. Zentr. 1911, **82**, I, 1089; Chem. Ztg. Rep. 1911, **35**, 203; Wag. Jahr. 1911, **57**, I, 422.

10. E. P. 3174, 1914; abst. J. S. C. I. 1915, **34**, 905.

of the sulfur is an old suggestion, and is described by O. Kohsel,¹ who reduced gypsum with coal to calcium sulfide, decomposed the latter with carbon dioxide, and burned the hydrogen sulfide to sulfur dioxide. The same process is described by C. Claus, W. Barbnoff and E. Hildt,² and the Badische Co.³

A number of other more or less meritorious processes have been described by W. Petrie,⁴ Houzé,⁵ P. Surcouf,⁶ Deacon,⁷ A. Sébillot,⁸ W. Hähner,⁹ Consortium f. Elektrochem. Ind.,¹⁰ O. Bender,¹¹ H. Kühne,¹² A. Coehn and H. Becker,¹³ W. Hallock,¹⁴ F. Cottrell,¹⁵ A. Reynoso,¹⁶ L. Wacker,¹⁷ A. Johnson,¹⁸ C. Jacobs,¹⁹ J.

1. Hannov. Mittheil. 1856, 135; abst. Wag. Jahr. 1856, **2**, 57; Poly. Centr. 1856, **22**, 1148.
2. D. R. P. 104188; abst. Zts. ang. Chem. 1899, **12**, 626; Chem. Centr. 1899, **70**, II, 800; Jahr. Chem. 1899, **52**, 420; Chem. Ztg. 1899, **23**, 725; Wag. Jahr. 1899, **45**, 354.
3. D. R. P. Anm. B. 79367.
4. E. P. 590, 1852.
5. Mon. ind. **7**, 65.
6. F. P. 310600, 1901; abst. Chem. Ztg. 1902, **26**, 252; Mon. Sci. 1902, **58**, 173.
7. Chem. Trade J. 1889, **5**, 193.
8. D. R. P. 109484; abst. Zts. ang. Chem. 1900, **13**, 421; Chem. Centr. 1900, **71**, II, 227; Chem. Ztg. 1900, **24**, 444; Wag. Jahr. 1900, **46**, I, 321; Mon. Sci. 1901, **57**, 17.
9. E. P. 717, 1854.
10. D. R. P. 157043; abst. Chem. Centr. 1905, **75**, I, 131; Chem. Ztg. 1904, **28**, 1212; Wag. Jahr. 1904, **50**, I, 292; Mon. Sci. 1905, **63**, 113; Chem. Zts. 1905, **4**, 122. F. P. 335496, 1903; abst. Chem. Zts. 1904, **3**, 279; Mon. Sci. 1904, **61**, 76.
11. D. R. P. 195810; abst. Zts. ang. Chem. 1908, **21**, 1371; Chem. Zentr. 1908, **79**, I, 1218; Jahr. Chem. 1905-1908, I, 1612; Chem. Ztg. Rep. 1908, **32**, 228; Mon. Sci. 1911, **75**, 82; Chem. Zts. 1908, **7**, 755.
12. E. P. 17520, 1908. D. R. P. 203541. F. P. 393461; abst. J. S. C. I. 1909, **28**, 982; Zts. ang. Chem. 1909, **22**, 267; Chem. Zentr. 1908, **79**, II, 1654; Jahr. Chem. 1905-1908, I, 1609; Chem. Ztg. Rep. 1908, **32**, 622; Wag. Jahr. 1908, **54**, I, 373; Mon. Sci. 1909, **71**, 134; 1912, **77**, 90; Chem. Zts. 1909, **8**, No. 1220.
13. D. R. P. 217722; abst. Wag. Jahr. 1910, **56**, I, 419; Zts. ang. Chem. 1910, **23**, 764; Chem. Zentr. 1910, **81**, I, 585; Jahr. Chem. 1910, **63**, I, 526; Chem. Ztg. Rep. 1910, **34**, 50; Mon. Sci. 1913, **79**, 158; Chem. Zts. 1910, **9**, No. 1774; Zts. Schiess. Spreng. 1910, **5**, 53.
14. U. S. P. 930471; abst. Mon. Sci. 1910, **73**, 81.
15. U. S. P. 866843, 866844; abst. Mon. Sci. 1908, **69**, 49.
16. E. P. 2181, 1874; abst. Dingl. Poly. 1876, **219**, 472. F. P. 10398, 1874.
17. E. P. 3183, 1895. D. R. P. Anm. W. 10532, 1894. W. 10591, 1895; abst. Jahr. Chem. 1897, **50**, 514; Chem. Ztg. 1896, **20**, 591; Mon. Sci. 1897, **50**, 30.
18. U. S. P. 659236. See also W. M. Johnson, U. S. P. 825057, 1906; abst. Chem. Ztg. Rep. 1906, **30**, 281; Mon. Sci. 1907, **67**, 12; Chem. Zts. 1906, **5**, 495.
19. U. S. P. 704831, 1902; abst. J. A. C. S. 1903, **25R**, 100; Mon. Sci. 1902, **58**, 184.

Kitsee,¹ G. Salom,² L. Bassett,³ W. Garroway,⁴ E. Riesenfeld,⁵ A. von Grätzel,⁶ G. Burnside and J. Anderson,⁷ H. Dercum,⁸ C. Hoepfner,⁹ The General Electric Co.,¹⁰ P. Askenasy and M. Mugdan,¹¹ J. Hannay,¹² E. Parnell and J. Simpson,¹³ and others.¹⁴

Electrolytic processes are described by E. Jungner,¹⁵ G. de Briailles,¹⁶ A. Fischer and G. Delmarcel,¹⁷ A. Friedländer,¹⁸ C. Boehringer & Sons,¹⁹ S. Emmens,²⁰ C. von Grabowski,²¹ H. Dawson,²² F. Freeth,²³ G. Gin,²⁴ J. Kessler,²⁵ G. Roge²⁶ and A. Scheurer-

1. U. S. P. 869094; abst. Mon. Sci. 1908, **69**, 50.
2. U. S. P. 755247; abst. J. A. C. S. 1904, **26R**, 435; Chem. Ztg. 1904, **28**, 363; Mon. Sci. 1904, **61**, 125.
3. E. P. 21475, 1907; abst. J. S. C. I. 1908, **27**, 906. F. P. 370170.
4. E. P. 1755, 1903; abst. J. S. C. I. 1904, **23**, 252.
5. D. R. P. 229274; abst. C. A. 1911, **5**, 2314; Zts. ang. Chem. 1911, **24**, 88; Chem. Zentr. 1911, **82**, I, 178; Chem. Ztg. Rep. 1911, **35**, 13; Wag. Jahr. 1911, **57**, I, 422.
6. D. R. P. 157767; abst. Zts. ang. Chem. 1905, **18**, 705; Chem. Centr. 1905, **75**, I, 702; Jahr. Chem. 1905-1908, I, 1623; Chem. Ztg. 1905, **29**, 223; Wag. Jahr. 1905, **51**, I, 405; Mon. Sci. 1905, **63**, 114; Chem. Zts. 1905, **4**, 270, 386.
7. E. P. 23605, 1913; abst. J. S. C. I. 1914, **33**, 1143.
8. E. P. 8299, 8300, 1900.
9. E. P. 19375, 1891; abst. Mon. Sci. 1897, **50**, 639.
10. E. P. 10881, 1904; abst. J. S. C. I. 1905, **24**, 503; Chem. Ztg. 1905, **29**, 1014; Mon. Sci. 1906, **65**, 138.
11. E. P. 14342, 1903; abst. J. S. C. I. 1903, **22**, 1085; Chem. Ztg. 1904, **28**, 1052; Mon. Sci. 1905, **63**, 52. U. S. P. 804515, 1905; abst. Chem. Zts. 1906, **5**, 17; J. A. C. S. 1906, **28R**, 342; Mon. Sci. 1906, **65**, 67.
12. E. P. 14247, 1886; abst. J. S. C. I. 1887, **6**, 729; J. Soc. Dyers Col. 1886, **2**, 810.
13. E. P. 14364, 1885; abst. J. S. C. I. 1886, **5**, 666; Chem. Centr. 1887, **58**, 423; Wag. Jahr. 1887, **33**, 488.
14. L. Droy, Belg. P. 277686, 1910.
15. E. P. 5223, 1908; abst. J. S. C. I. 1909, **28**, 529.
16. E. P. 22434, 1908; abst. J. S. C. I. 1909, **28**, 1199. F. P. 393665; abst. Mon. Sci. 1909, **71**, 135. U. S. P. 928864. Belg. P. 211215, 1908.
17. Bull. Soc. Chim. Belg. 1910, **24**, 236; abst. J. S. C. I. 1910, **29**, 694.
18. D. R. P. 127985; abst. Zts. ang. Chem. 1902, **15**, 182; Chem. Centr. 1902, **73**, I, 504; Jahr. Chem. 1902, **55**, 356; Chem. Ztg. 1902, **26**, 186; Wag. Jahr. 1902, **48**, I, 305; Mon. Sci. 1902, **58**, 153; Chem. Zts. 1902, **1**, 450, 473.
19. D. R. P. 117129; abst. Zts. ang. Chem. 1901, **14**, 166; Chem. Centr. 1901, **72**, I, 285; Jahr. Chem. 1901, **54**, 196; Chem. Ztg. 1900, **24**, 90; Wag. Jahr. 1901, **47**, I, 518; Mon. Sci. 1901, **57**, 152; Chem. Zts. 1902, **1**, 32.
20. E. P. 10011, 1885; abst. J. S. C. I. 1886, **5**, 455.
21. E. P. 15218, 1893; D. R. P. 71917; abst. Wag. Jahr. 1894, **40**, 371; Zts. ang. Chem. 1893, **6**, 700; Ber. 1894, **27**, 175; Mon. Sci. 1894, **44**, 55.
22. E. P. 127677, 1917; abst. C. A. 1919, **13**, 2421.
23. E. P. 117649; abst. J. S. C. I. 1918, **37**, 579-A.
24. Belg. P. 163688, 1903.
25. E. P. 5016, 1886; abst. J. S. C. I. 1887, **6**, 292.
26. E. P. 124988, 1918; abst. C. A. 1919, **13**, 1748; J. S. C. I. 1919, **38**, 323-A.

Kestner,¹ and are among the more meritorious processes.

Sulfuric Acid and Nitrogen Oxides.² Reference has already been made to the rôle played by the nitrogen oxides in the chamber process for the manufacture of sulfuric acid. It is believed that the oxides act in a cyclic manner, involving the intermediate formation of nitrosylsulfuric acid, $\text{SO}_2(\text{OH})\text{ONO}$. The reactions of nitrogen oxides and sulfuric acid have been studied by R. Weber,³ C. Winkler,⁴ and G. Lunge and his pupils.⁵

Nitrous and nitric oxides are practically insoluble in sulfuric acid, and do not appear to chemically react with it. The solubility of NO in sulfuric acid has been measured by J. Kolb,⁶ and by G. Lunge.⁷ The latter states that 1 liter of concentrated sulfuric acid absorbs, at the ordinary temperature, only 0.0593 gm., or 35 cc. NO, and acid of sp. gr. 1.500 absorbs only half that amount.

In the presence of oxygen, nitric oxide is readily absorbed by concentrated sulfuric acid, but it is then converted, before absorption, into higher nitrogen oxides, N_2O_3 and NO_2 . If the gases after mixing are rapidly brought in contact with the acid, nothing but nitrosylsulfuric acid is formed, even with excess of oxygen. The higher nitrogen oxide formed, therefore, behaves as though it were all nitrous anhydride, N_2O_3 , although only traces of this can exist in the gaseous state under the conditions of the experiment⁸; $2\text{SO}_2(\text{OH})_2 + \text{N}_2\text{O}_3 = 2\text{SO}_2(\text{OH})\text{ONO} + \text{H}_2\text{O}$. If, however, the mixture of nitric oxide with oxygen or air is

1. Dingl. Poly. 1885, **255**, 87; abst. J. S. C. I. 1885, **4**, 210.

2. Clement and Desormes, Ann. Chim. 1806, **59**, 329; N. Gehl, **4**, 457. Davy, Chem. ord. philos. researches chiefly concerning nitrous oxide, London, 1800.

3. J. prakt. Chem. 1862, **85**, 423; 1867, **100**, 37; Pogg. Ann. 1864, **123**, 341; 1866, **127**, 543; 1867, **130**, 277; Dingl. Poly. 1863, **167**, 453.

4. "Researches on the Chemical Processes going on in the Gay-Lussac Towers," Freiberg, 1867.

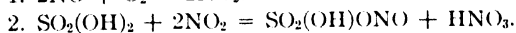
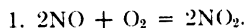
5. Ber. 1877, **10**, 1073, 1432; 1878, **11**, 434, 1229. Dingl. Poly. 1878, **228**, 70, 548, 553; 1879, **233**, 63. Ber. 1879, **12**, 357, 1058; 1881, **14**, 2188, 2196; 1882, **15**, 488, 495. Chem. Ind. 1884, **7**, 5. J. S. C. I. 1885, **4**, 31, 447. Ber. 1885, **18**, 1376, 1384, 1391. J. C. S. 1885, **47**, 457, 465. Ber. 1888, **21**, 67, 3223. Zts. ang. Chem. 1889, **2**, 265, 385; 1890, **3**, 195; 1899, **12**, 393.

6. Bull. Soc. Ind. Mulhouse, 1872, 225; Bull. Soc. Chim. 1873, **20**, 521.

7. J. S. C. I. 1885, **4**, 447; 1886, **5**, 82. Ber. 1885, **18**, 1391; 1886, **19**, 111.

8. See O. Witt, Ber. 1878, **11**, 2188. W. Ramsay and J. Cundall, J. C. S. 1885, **47**, 187, 672. G. Lunge, J. C. S. 1885, **47**, 457; Zts. anorg. Chem. 1894, **7**, 209. H. Dixon and J. Peterkin, Proc. Chem. Soc. 1899, 115. H. Brereton, H. and M. Baker, J. C. S. 1907, **91**, 1862. J. Biehringer and W. Borsum, Ber. 1910, **43**, 1402; abst. J. S. C. I. 1910, **35**, 961.

allowed to stand for a greater or less time before bringing it into contact with the acid, nitrogen peroxide is formed, which yields nitric acid in contact with sulfuric acid, as well as nitrosylsulfuric acid.



The absorption is then less rapid than in the previous case, and the reaction is reversible. The importance of these facts in connection with the Gay-Lussac tower has already been pointed out.

The compound formed by the absorption of nitrous fumes in concentrated sulfuric acid may be obtained in a solid state. It was formerly considered to be nitrosulfonic acid, $\text{SO}_2(\text{OH})\text{NO}_2$, but is now regarded as nitrosylsulfuric acid, $\text{SO}_2(\text{OH})\cdot\text{O}\cdot\text{NO}$, and is best prepared by passing sulfur dioxide into well-cooled fuming nitric acid until the whole is pasty, and drying on a porous tile over sulfuric acid. It forms quadrangular prisms, but is often obtained in the form of feathery crystals. These melt at 73° (Weltzein) or 120° – 130° (Gaultier de Claubry), but with decomposition and evolution of red fumes of nitrogen oxides.

An anhydride of nitrosylsulfuric acid, $\text{N}_2\text{O}_3\cdot 2\text{SO}_3$, or $\text{NO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}$, is formed by mixing liquid sulfur dioxide and nitrogen peroxide, or sulfur trioxide and nitric oxide, or by heating sulfur trioxide with nitrogen peroxide.

The action of water on chamber crystals has already been described in connection with the Glover tower, and its behavior towards sulfuric acid of various concentrations mentioned. No appreciable decomposition occurs with acids of higher sp. gr. than 1.55; below this, rapid decomposition occurs.

The use of chamber crystals instead of niter for supplying nitrogen oxides to chambers has been proposed;¹ they are also used in making azo-dyes and other azo-compounds.² When they are heated with common salt, nitrosyl chloride, NOCl , is formed.

By the action of sulfur dioxide on nitrous vitriol, a blue or purple acid is formed, the composition of which has been the subject of much discussion.³ It appears to be nitroso-sulfuric

1. Soc. le Nitrogene, F. P. 404071, 1909.

2. J. Pabst and A. Girard, E. P. 2811, 1878.

3. W. Manchot, Zts. ang. Chem. 1910, **23**, 2112; 1911, **24**, 13; 1912,

acid, H_2SNO_6 , but has not been isolated in a pure state. It is supposed to play some part in the reactions of the chamber process, but its rôle is purely hypothetical.

Recovery of Waste Sulfuric Acid. Many processes have been proposed to recover sulfuric acid from various manufacturing residues.¹

The acid tar from the refining of petroleum and oils contains considerable amounts of sulfuric acid. The Chemische Fabrik A. G.² dilute with water in the proportion of one of water to one of acid, and allow to settle. The lower layer contains the acid, and may be freed from the remaining resinous impurities by washing with carbolic acid or other similar bodies, and can then be used in decomposing sodium phenate or cresate. The acid is preferably converted into ammonium sulfate by neutralizing with ammonia after adding 5% of tar bases, the resinous impurities floating to the surface with these. R. Ostrejko³ throws out the tar with water and then decolorizes with specially prepared charcoal. J. Fleischer⁴ introduces the acid into clay vessels, which are then placed in water. Pure sulfuric acid diffuses into the water, while the acid content of the tar decreases. G. Stolzenwald⁵ dilutes the waste acid with water, heats in covered lead pans and leads the vapors to condensers in which oil and water separate. The residue is run into a vat, where it is cooled. The resin and tar separate on the surface as a solid cake, while acid of 55° Bé., containing only a small amount of tarry matter,

25, 1055; abst. C. A. 1911, 5, 1663; 1912, 6, 3312. P. Sabatier, *Compt. rend.* 1896, 122, 1417; abst. *Jahr. Chem.* 1896, 49, 384. F. Raschig, *Zts. ang. Chem.* 1910, 23, 2248; 1912, 25, 1055. J. Buraczewski and S. Zbijewski, *Oesterr. Chem. Ztg.* 1911, 14, 235; abst. J. S. C. I. 1911, 30, 1208; C. A. 1912, 6, 1058. A. Girard and J. Pabst, *E. P.* 3584, 1881; abst. *Chem. Ind.* 1881, 4, 431.

1. F. Farrar and F. Gill, *U. S. P.* 206309. F. Gardair and T. Gladysz, *E. P.* 5030, 1882. M. Barrett, *E. P.* 1394, 1870. T. Jackson, *E. P.* 1583, 1874. J. Mackenzie, *E. P.* 13907, 1915; abst. J. S. C. I. 1916, 35, 838. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, *Norw. P.* 23068. I. Pfeiffer and J. Fleischer, *Aust. P.* 43239, 1910. A. Perrisat, *U. S. P.* 204244, 1878. Rheinische Gelatine-Werke G. m. b. H., *F. P.* 336507, 1903. See also Y. Manuro, *Chem. Techn. Japan*, 1919, 3, 25; abst. C. A. 1919, 13, 1372.

2. *E. P.* 9614, 1885; abst. J. S. C. I. 1886, 5, 160.

3. *E. P.* 18040, 1900.

4. *U. S. P.* 182246, 1906; abst. C. A. 1907, 1, 2333.

5. D. R. P. 212000, 213589, 1908; abst. C. A. 1910, 4, 239; *Wag. Jahr.* 1909, 55, II, 28; *Zts. ang. Chem.* 1909, 22, 1692, 2249; *Chem. Zentr.* 1909, 30, II, 484, 1094; *Chem. Ztg. Rep.* 1909, 33, 506; *Zts. Schiess. Spreng.* 1909, 4, 292, 294. *Chem. Ztg.* 1908, 32, 1017; abst. C. A. 1909, 3, 230.

remains. The Steaua Romana Petroleum Ges., Regensburg¹ run the acid continuously into boiling sulfuric acid while introducing a current of air. Organic matters are destroyed, and the vapors are collected in a suitable apparatus. The addition of sulfuric acid is only necessary in starting the process. W. van Tienen² adds water and heats the mixture to 140°–165° under a pressure of 7 atm. The water added must suffice to dilute the remaining acid to a density not more than 52° Bé. F. Bühler³ exposes the waste acid to hot gases free from oxygen, at a temperature of 273° and upwards, by means of a rotating drum dipping into it. The coke residue left on the drum is removed by a scraper, and also recovered. J. Hausman⁴ states that the recovered acids contain about 2% of sulfonic acids. A. Gellen⁵ heats the acid with steam coils in a special apparatus, and obtains a separation into acid and oils. The Sprengstoff A. G. Carbonit⁶ pass the gases and vapors over water or dilute nitric acid, when solid organic matters solidify. F. Bräunlich⁷ runs the acid tar slowly into fused sodium bisulfate, preferably kept in motion, at a temperature above the boiling point of sulfuric acid. The presence of a catalyzer, e. g., copper sulfate, increases the action. Acid which has been diluted with water may also be treated. C. Still⁸ warms the waste acid and feeds it to a steam jet blower worked by steam under pressure, which may be superheated. The intimate mixture of steam and waste acid is delivered into a vessel surmounted by a dome. The acid collects in this vessel, and the acid resins and other solid impurities settle out as a friable mass. The steam passes to a condenser and washer, to

1. D. R. P. 221615, 1909; abst. C. A. 1910, **4**, 2718; Chem. Zentr. 1910, **81**, I, 1818; Jahr. Chem. 1910, **63**, I, 526; Chem. Ztg. Rep. 1910, **34**, 275; Wag. Jahr. 1910, **56**, I, 70; Mon. Sci. 1914, **81**, 76.

2. E. P. 23368, 1910; abst. C. A. 1911, **5**, 3152; J. S. C. I. 1911, **30**, 409.

3. D. R. P. 287755; abst. J. S. C. I. 1916, **35**, 176; Chem. Zentr. 1915, **86**, II, 930; Chem. Ztg. Rep. 1915, **39**, 448; Zts. ang. Chem. 1915, **28**, II, 582.

4. Petroleum, 1911, **6**, 2301; abst. J. S. C. I. 1911, **30**, 1149.

5. U. S. P. 1063025; abst. C. A. 1913, **7**, 2468; Chem. Ztg. Rep. 1913, **37**, 478.

6. E. P. 11854, 1913; abst. C. A. 1914, **8**, 2807; J. S. C. I. 1913, **32**, 1130; Chem. Ztg. Rep. 1914, **38**, 299.

7. E. P. 2695, 1913; abst. J. S. C. I. 1913, **32**, 826; C. A. 1914, **8**, 2606. D. R. P. 267873; abst. C. A. 1914, **8**, 998; Zts. ang. Chem. 1914, **27**, 50; Chem. Zentr. 1914, **85**, I, 198; Chem. Ztg. Rep. 1913, **37**, 694; Wag. Jahr. 1913, **59**, I, 381.

8. D. R. P. 291775; abst. J. S. C. I. 1916, **35**, 829; Zts. ang. Chem. 1916, **29**, 271; Chem. Zentr. 1916, **87**, I, 1048; Chem. Ztg. Rep. 1916, **40**, 217.

remove SO_2 . J. and, A. Blowski¹ dilute with water and rapidly distil to minimize reduction of the sulfuric acid by organic matter present. C. van Vooghut² dilutes with water to about 52° Bé., and places in a lead-lined, steam-jacketed autoclave. Carbon dioxide is forced in till the pressure rises to 7 atm., then steam into the jacket of the autoclave until the pressure within rises to 10 atm. The heating is maintained for 2 hours, when the acid will have separated from the tar. The acid and tar are blown out separately, the CO_2 being washed and re-used. Kroupa³ runs the acid tar in a finely divided state over heated fire-proof and acid-proof materials, with admixture of air. Other methods have been proposed.⁴

Waste acid from the manufacture of benzol may also be recovered. The Phoenix A. G., Gelsenkirchen,⁵ mix the waste acids with ammonia water, to obtain ammonium sulfate. A. Gasser⁶ agitates the acid vigorously with a current of warm compressed air, which causes the impurities to become agglomerated and can be skimmed off from the surface of the acid. The air may be that used for cooling coke oven brickwork, and it is preferably dried with quicklime.⁷

M. Lemaitre⁸ treats acid from the manufacture of dynamite with steam superheated to 300°-400°, or with hot air in connection with dilute sulfuric acid at 200°. The acid after denitration still contains 2½%-3% nitrosulfonic acid, which, after concen-

1. U. S. P. 1186373, 1916; abst. J. S. C. I. 1916, **35**, 839; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 181.

2. E. P. 12363, 1915; abst. J. S. C. I. 1916, **35**, 528. D. R. P. 292728; abst. Zts. ang. Chem. 1916, **29**, 352; Chem. Ztg. Rep. 1916, **40**, 285.

3. Aust. P. 67116; abst. Oest. Chem. Ztg. 1917, **20**, 14.

4. Zdaska, D. R. P. Ann. Z. 8310. P. and F. Murphy, U. S. P. 1094861. A. Kützer, E. P. 27977, 1913. J. Blowski, U. S. P. 1186373, 1916. Farbenfabr. vorm. F. Bayer & Co., Aust. P. 66211; abst. Oest. Chem. Ztg. 1917, **20**, 14. E. Clark, U. S. P. 232685, 1880. Chem. Fabrik Akt. Ges. Hamburg, D. R. P. 34947, 36372; abst. Wag. Jahr. 1886, **32**, 445, 446; 1887, **33**, 112. T. Dotterer, U. S. P. 270763; abst. J. S. C. I. 1883, **2**, 178.

5. D. R. P. 289162; abst. J. S. C. I. 1916, **35**, 422; Zts. ang. Chem. 1916, **29**, 27; Chem. Zentr. 1916, **37**, I, 193; Chem. Ztg. Rep. 1916, **40**, 18. D. R. P. 289524; abst. J. S. C. I. 1916, **35**, 422; Zts. ang. Chem. 1916, **29**, 69; Chem. Zentr. 1916, **37**, I, 193; Chem. Ztg. Rep. 1916, **40**, 39.

6. D. R. P. 272130; abst. J. S. C. I. 1914, **33**, 587; Oest. Chem. Ztg. 1917, **20**, 14.

7. C. Dreyman, D. R. P. 233517; abst. Wag. Jahr. 1911, **57**, I, 112. Cf. H. de Groussilliers, D. R. P. 43900; abst. Wag. Jahr. 1888, **34**, 76.

8. Mon. Sci. 1913, **78**, 217; abst. Chem. Ztg. Rep. 1913, **37**, 478.

tration to 92%-94% acid, is reduced to 0.15%. T. Jones¹ cools this acid to freeze out the nitroglycerol, which is separated centrifugally. The acid may then be treated with superheated steam until red fumes are evolved, when hot air is substituted for the steam. The Saltpetersäure-Industrie Ges., Gelsenkirchen, have also devised a process for the recovery of these waste acids.²

E. Natho³ treats acids contaminated with inorganic salts with equivalent quantities of calcium carbonate and fine sand. The precipitate, consisting of gypsum and sand, is heated in an autoclave to 600°-800°. The sulfuric acid evolved is taken up in water.

Methods for the treatment of waste pickle have been described. E. Howl and F. Perry⁴ evaporate until the free acid attains a concentration of about 75%, when the major portion of the ferrous sulfate separates in the anhydrous form. R. Lavender, J. Richards and D. Williams⁵ filter, evaporate and allow to crystallize. The crystals are heated in fireclay retorts, and the acid vapors utilized in a chamber plant. T. Parker and A. Robinson⁶ evaporate to sp. gr. 1.4-1.5 in contact with iron. Strong sulfuric acid is added, resulting in the precipitation of anhydrous ferrous sulfate, which may be distilled for the production of fuming acid. T. Parker⁷ proposes to regenerate the acid by electrolysis, with deposition of iron on the cathode. F. Anderson⁸ precipitates with milk of lime, allows the precipitate of ferrous hydroxide, calcium sulfate, and a little excess of lime, to subside, and pumps it to a filter press. The cakes are exposed to air for

1. E. P. 304, 1878; abst. Chem. Ind. 1878, **1**, 108; Wag. Jahr. 1880, **26**, 376.

2. E. P. 18113, 1913; abst. J. S. C. I. 1914, **33**, 790.

3. D. R. P. 262466, 1912; abst. C. A. 1913, **7**, 3534; Zts. ang. Chem. 1913, **26**, 477; Chem. Zentr. 1913, **84**, 11, 552; Chem. Ztg. Rep. 1913, **37**, 438; Wag. Jahr. 1913, **59**, I, 381; Zts. Schiess. Spreng. 1913, **8**, 297.

4. E. P. 5830, 1914; abst. J. S. C. I. 1915, **34**, 423; Chem. Ztg. Rep. 1915, **39**, 336; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 110. F. Fireman, U. S. P. 1287939, 1918; abst. C. A. 1919, **13**, 417. Chim. Ind. 1920, **3**, 206. W. Pughsley, E. P. 2259, 1867; 4373, 1874. Steaua Romana Petroleum Ges., D. R. P. 224566; abst. Wag. Jahr. 1910, **56**, I, 71; C. A. 1911, **5**, 195; Zts. ang. Chem. 1910, **23**, 2105; Chem. Zentr. 1910, **81**, 11, 606; Chem. Ztg. Rep. 1910, **34**, 475; Mon. Sci. 1914, **81**, 88; Jahr. Chem. 1910, **63**, I, 507.

5. E. P. 3182, 1878; abst. Wag. Jahr. 1879, **25**, 294; J. A. C. S. 1879, **1**, 501.

6. E. P. 10554, 1889.

7. E. P. 9632, 1889; abst. J. S. C. I. 1890, **9**, 435.

8. E. P. 3505, 1913; abst. C. A. 1914, **8**, 2587; J. S. C. I. 1914, **33**, 312.

a few days, when finely divided ferric hydroxide is formed, which may be used in the purification of coal gas.

The by-products resulting from the manufacture of sulfuric acid are burnt pyrites, zinc, iron, copper, selenium, thallium, silver, etc.; a discussion of their recovery and utilization being beyond the scope of this work. For detailed information on this subject the subjoined sources may be consulted.¹

Preparing Mixtures of Oleum and Sulfuric Acid. J. Prats² gives a formula for preparing definite mixtures of oleum and ordinary acid. Let a = quantity of oleum, containing $h\%$ SO_3 , required; x = weight of oleum of given concentration $k\%$ free SO_3 ; y = weight of ordinary sulfuric acid containing $s\%$ H_2SO_4 . Then:

$$1. x = a \times \frac{9h + 40(100 - s)}{9k + 40(100 - s)}$$

$$2. y = a \times \frac{9(k - h)}{9k + 40(100 - s)}$$

If ordinary acid of sixty-six degrees Baumé is used, the

1. U. S. Min. Resources, 1911, I, 977. H. Lorentzen, D. R. P. 254253, 254840; abst. Wag. Jahr. 1912, **56**, I, 202. Brück, Kretschel & Co., F. P. 457245; abst. C. A. 1914, **8**, 2145; D. R. P. 271822; abst. C. A. 1914, **8**, 2338. W. Buddacius, D. R. P. 278064. D. R. P. 273277, abst. Chem. Zentr. 1914, **85**, I, 1719; C. A. 1914, **8**, 2671. Hochofenwerk Luebeck Akt. Ges., D. R. P. 280849; abst. J. S. C. I. 1915, **34**, 650; C. A. 1915, **9**, 1686. C. Hoepfner, D. R. P. 66096, abst. Ber. 1893, **26**, 253; Wag. Jahr. 1892, **38**, 222. Internationale Wasserstoff Akt. Ges., D. R. P. 220889, 244732; abst. Chem. Zentr. 1912, **83**, I, 1062; C. A. 1912, **6**, 2232. P. Klason and H. Mellquist, Swed. P. 35177. H. Koelsch, Chem. Ztg. 1913, **37**, 753; abst. Chem. Zentr. 1913, **84**, II, 540; J. S. C. I. 1913, **32**, II, 729; C. A. 1913, **7**, 3583. J. McFetridge, U. S. P. 1045723, 1912; abst. J. S. C. I. 1913, **32**, 24; C. A. 1913, **7**, 685. MacKay Copper Process Co., D. R. P. 278153; abst. C. A. 1915, **9**, 762. Metals Research Co., D. R. P. 293967. G. Polysius, D. R. P. 277854. A. Ramen, D. R. P. 293541. J. Savelsberg, D. R. P. 268093, abst. C. A. 1914, **8**, 1563. D. R. P. 210742, abst. Chem. Zentr. 1909, **80**, II, 163. D. R. P. 241464, addn. to D. R. P. 210742. D. R. P. 261307, abst. Chem. Zentr. 1913, **84**, II, 200, 398; J. S. C. I. 1913, **32**, 1011; C. A. 1913, **7**, 3108. D. R. P. 261800, addn. to D. R. P. 261307; abst. Chem. Zentr. 1913, **84**, II, 398. O. Spinzig and A. Wannag, D. R. P. 255454; abst. Chem. Zentr. 1913, **84**, I, 453; J. S. C. I. 1913, **32**, 241. P. Uebbing, Metal. and Erz. 1913, **10**, 607; abst. Zts. ang. Chem. 1914, **27**, 90. G. VanArsdale, U. S. P. 1119477, 1119478, 1914; abst. J. S. C. I. 1915, **34**, 36. Van Endert and Koenig, Chem. Ztg. Rep. 1914, **38**, 124. C. Weeks, U. S. P. 1048247, 1912; abst. J. S. C. I. 1913, **32**, 85; C. A. 1913, **7**, 680; Mon. Sci. 1913, **79**, 99. W. Weldon, E. P. 5607, 1882; abst. J. S. C. I. 1883, **2**, 415; Ber. 1884, **17**, 33; Chem. Ind. 1884, **7**, 45; Chem. Tech. Rep. 1884, **23**, I, 217.
2. Chem. Ztg. 1910, **34**, 264; abst. C. A. 1910, **4**, 1796. Eighth Intl. Cong. Appl. Chem. 1912, **1**, 395.

formula may readily be abridged so as to read as follows:

$$1a. x = a \times \frac{h + 20}{k + 20}$$

$$2a. y = a \times \frac{k - h}{k + 20}.$$

A graphic method of determining the proportions of oleum and C. O. V. for mixing is described by E. Craven.¹ Two parallel side scales are provided with a slide between them. One of the scales is marked with C. O. V. concentrations in per cents. H_2SO_4 , the other with oleum strengths in per cents. SO_3 . Unit lengths on each side scale correspond with the same percentage difference of SO_3 . The slide is marked with an inclined line divided into 100 parts, joining two corresponding points on the scales, e. g., 100% H_2SO_4 and 81.63% SO_3 . The slide is set with one end of the line against the desired strength of acid and the percentage strengths of the storage tanks of oleum and C. O. V. joined by a line. The intersection point of the divided line gives the reading for the relative proportions of oleum and C. O. V. to be mixed. A similar arrangement is described by H. Moore.²

The Properties of Pure Sulfuric Acid (Monohydrate). Pure sulfuric acid, generally called monohydrate, i. e., $SO_3 \cdot H_2O$, has the formula H_2SO_4 , or $SO_2(OH)_2$. It may be regarded as containing 81.63% SO_3 and 18.37% H_2O . It is a colorless oily liquid, without smell. Its sp. gr. at 0° is 1.853; at 15°, compared with water at 4°, has been given as: 1.8384 (G. Lunge and P. Naef), 1.8378 (Schertel), 1.8372 (Marignac, F. Kohlrausch and D. Mendeléeff³). The specific gravity varies to the extent of ± 0.001 per degree C.

Pure monohydrate solidifies on cooling to about 0° C., forming large, flat crystals which melt at 10.5°. They remain super-fused considerably below this temperature, but solidify on agitation, or on the addition of a trace of solid.⁴ The acid begins to

1. Chem. News, 1918, **117**, 217; abst. J. S. C. I. 1918, **37**, 412-A; C. A. 1919, **13**, 249.

2. J. Ind. Eng. Chem. 1912, **4**, 677; abst. C. A. 1913, **7**, 1587.

3. Ber. 1884, **17**, 1748, 2536, 2711; abst. Bull. Soc. Chim. 1885, **44**, 197; Jahr. Chem. 1884, **37**, 76.

4. The Chem. Fabrik Griesheim (D. R. P. 24402; abst. Wag. Jahr. 1883, **29**, 266) make use of this property of sulfuric acid to produce pure monohydrate. See also W. Jorissen, Chem. Weekblad. 1913, **10**, 962; abst. C. A. 1914, **8**, 3540; Chem. Zentr. 1914, **35**, I, 105.

boil at 290° , but the boiling point rises to 338° . This change is due to the dissociation of the acid: $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_3$; the vapor is a mixture of H_2SO_4 , SO_3 and steam. This dissociation begins at as low a temperature as 30° – 40° , when slight fumes of SO_3 are given off by the pure monohydrate. Thus the latter cannot be obtained by distillation, but only by adding the requisite amount of the anhydride to the pure concentrated acid. It may also be obtained by crystallization of the latter by cooling.

The vapor of sulfuric acid is almost completely dissociated. The theoretical vapor density for H_2SO_4 is 3.386 (air = 1); that for the completely dissociated mixture, 1.693. Deville and Troost at 444° found the vapor density 1.74.¹

Transportation of Sulfuric Acid. This acid is often transported, especially in relatively small amounts, in large glass bottles holding about 15 gallons, called carboys. These are protected by enclosure in baskets or boxes, and closed by stoneware stoppers, which may be dipped in melted sulfur and put in place before the sulfur solidifies. Plaster of paris is also used for keeping the stoppers tight, but soon becomes soft in contact with the acid. The baskets are easily eaten away by splashing of acid, and the bottoms fall out first. In England, baskets of strong hoop iron, or iron from cotton bales, well tarred, are used, and these form very durable and clean packings. In America, cubical boxes are preferred, kept together by iron hoops and packed with marsh hay. Straw is used in many cases, but infusorial earth is not attacked by acid. In France large stoneware jars are used, which are encased in baskets when shipping.

For transporting large amounts of acid, tank wagons or cars are used. These are of wrought iron, which resists the action of oil of vitriol not weaker than 130° Tw., provided this contains no nitrous compounds, and air is excluded. The tanks are usually boiler-shaped, of as high as 50 tons capacity. The thickness of the plate is $\frac{3}{8}$ to $\frac{7}{16}$ in. for acids down to 140° Tw., and $\frac{5}{16}$

1. W. Dittmar, Chem. News, 1869, **20**, 258. G. Oddo and G. Anelli, Gazz. chim. ital. 1911, **41**, 552; Chem. Ztg. 1911, **35**, 846. D. Lichty, J. A. C. S. 1908, **30**, 1834; abst. J. S. C. I. 1909, **28**, 20. A. Hantzsch, Zts. physik. Chem. 1907, **61**, 257; Chem. Ztg. 1908, **32**, 1240. H. Armstrong and F. Worley, Proc. Roy. Soc. 1914, **90A**, 73; abst. J. S. C. I. 1914, **33**, 900. The reduction of sulfuric acid by carbon monoxide is discussed by J. Milbauer, Chem. Ztg. 1918, **42**, 313; abst. C. A. 1918, **12**, 2290; J. S. C. I. 1918, **37**, 404-A.

in. for chamber acid. The plates must be carefully riveted and tightly caulked. Corrosion occurs when the acid is in contact with air, so that the tanks should always be kept closed.¹ In the United States sulfuric acid is transported in 100-gallon, lead-lined drums.

Special containers for carboys have been described,² as well as arrangements for filling and closing the same.³

The transport of sulfuric acid by water is becoming increasingly important. For overseas transport, wooden boxes lined with lead are often used. The boats themselves may be used on canals if lined with lead.⁴ It has been proposed to soak up the acid in kieselguhr,⁵ loam or clay,⁶ or to mix the acid with anhydrous sodium or magnesium sulfate.⁷ Rules for the transportation of oleum have been made by the United States Steamboat Inspection Service.⁸ The maritime transport of sulfuric acid has been discussed by A. Hutin⁹ and Maurcourt.¹⁰ Careless packing can lead to serious accidents.¹¹

Properties of Sulfuric Acid. The ordinary concentrated sulfuric acid (C. O. V.) usually contains about 98% H_2SO_4 . It is assumed that liquid acids containing water, contain hydrates of H_2SO_4 . Many of these are assumed to have been ob-

1. R. Nörrenberg, *Chem. Ind.* 1896, **19**, 553; abst. *J. S. C. I.* 1897, **16**, 141. W. Balmain and W. Menzies, *E. P.* 97, 1870. H. Rabe, *Zts. ang. Chem.* 1911, **24**, 403. T. Oppler, *Chem. Ind.* 1889, 528.
2. H. Gaden, *E. P.* 7837, 1915; abst. *J. S. C. I.* 1915, **34**, 1197. Pfeffer, *Zts. ang. Chem.* 1908, **21**, 98, 104. Aktienges. f. Anilinfabrikation, *D. R. P.* 8350; abst. *Wag. Jahr.* 1880, **26**, 236. A. Mauser, *E. P.* 11695, 21986, 1902. C. Garneri, *E. P.* 3190, 1883; abst. *J. S. C. I.* 1884, **3**, 173.
3. E. Junckers, *Chem. Ztg.* 1902, **26**, 582.
4. J. Holden, *E. P.* 3805, 1877; abst. *Chem. Ind.* 1878, **1**, 181. Kuhlmann, *Chem. Ind.* 1879, **2**, 333.
5. Vorster & Grüneberg, *D. R. P.* 24748; abst. *Wag. Jahr.* 1883, **29**, 356; *Mon. Sci.* 1884, **26**, 510. I. McDougall, *E. P.* 1439, 1892.
6. P. Rippert, *E. P.* 8752, 1900. See W. Nichols, *U. S. P.* 175734, 1876.
7. W. White and A. Rickman, *E. P.* 17095, 1887; abst. *J. S. C. I.* 1888, **7**, 845. See also *E. P.* 17796, 1891; abst. *Chem. Centr.* 1893, **64**, 1, 630. P. Claes, *Belg. P.* 143961, 1899. *F. P.* 318745, 1902; abst. *Chem. Zts.* 1903, **2**, 273. A. Rickman, *D. R. P.* 45723; abst. *Wag. Jahr.* 1889, **35**, 389.
8. June, 1915; abst. *Chem. Trade J.* 1915, **57**, 104.
9. *Rev. chim. ind.* 1918, **27**, 7; abst. *C. A.* 1918, **12**, 1109. See also L. Couher, *Belg. P.* 127343, 1897.
10. Engrais, **27**, 988; abst. *C. A.* 1912, **6**, 2296.
11. Oil, Paint and Drug. Rep. Mar. 15, 1915; abst. *J. S. C. I.* 1915, **34**, 350. In this connection see R. Jordan, *D. R. P.* 280863, 1913; abst. *J. S. C. I.* 1915, **34**, 704. Control of emergencies arising from the manufacture or handling of acids is discussed by F. Carulla, *J. S. C. I.* 1902, **21**, 226.

tained by cooling the solutions, particularly by D. Mendeléeff and S. Pickering, but the researches of R. Knietsch¹ have shown that the only definite hydrates of sulfur trioxide are $2\text{SO}_3 \cdot \text{H}_2\text{O}$, $\text{SO}_3 \cdot \text{H}_2\text{O}$ and $\text{SO}_3 \cdot 2\text{H}_2\text{O}$. The evidence for the other supposed hydrates is no longer admitted by modern physical chemistry, and they are undoubtedly only eutectic mixtures.

The hydrates $2\text{SO}_3 \cdot \text{H}_2\text{O}$ and $\text{SO}_3 \cdot \text{H}_2\text{O}$ have already been described. The dihydrate of sulfur trioxide, $\text{SO}_3 \cdot 2\text{H}_2\text{O}$, or $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is formed by cooling rather more dilute acid, say that of 144°Tw. , containing 84.44% monohydrate and 15.52% water, or 68.97% anhydride and 31.03% water. It melts at $+8^\circ$, but remains superfused, and only solidifies below 0° . The crystals of this hydrate, which are large hexagonal prisms with hexagonal pyramidal ends, may separate from carboys of 144°Tw. acid if kept in a cold place, and crack them. Such acid therefore should always be stored in a warm locality. Stronger, or weaker acid may be exposed to winter weather without solidifying. On heating to 205° – 210° , the liquid loses the additional molecule of water, and forms ordinary oil of vitriol.

As stated above, the strongest acid which can be obtained by boiling ordinary oil of vitriol contains 98% H_2SO_4 . This acid solidifies a little below 0° , but shows superfusion in a high degree. It boils at 338° (Marignac), 315° – 317° (Pfaundler and Pöhl), the former observation being usually considered as correct. The acid if boiled at the atmospheric or lower pressure bumps violently, but may be avoided by placing bits of platinum foil or wire in the retorts. Dittmar states it is best to lead a slow current of air through the boiling acid. Above atmospheric pressure boiling occurs quietly.

The acid of 98% strength (98.3% according to Lunge) is an acid of maximum boiling point, as was shown by Knietsch, corresponding with 330° . The vapor pressure at 100° of this acid is zero; the density is a maximum; the electrical resistance also begins to increase sharply at this point, reaching a maximum at the monohydrate. This acid also absorbs the vapor of sulfur trioxide very readily, a fact made use of in the manufacture of oleum.

Although the general results of Knietsch are probably more

1. Ber. 1901, **34**, 4089. See T. Sullivan, Chem. Met. Eng. 1919, **21**, 511; abst. C. A. 1920, **14**, 207.

or less correct, it is necessary to observe that more recent work has thrown considerable doubt on the accuracy of the results obtained by this observer. The thermal data, in particular, must now be regarded as quite untrustworthy.

Ordinary "rectified oil of vitriol" (R. O. V.) usually contains less than 98% H_2SO_4 . The usual O. V., formerly called 170° Tw., but really 168° Tw., varies from 96% to 93% or 92% H_2SO_4 . The density is not a reliable criterion of the strength at this point, since a large difference of strength produces only a small change of density. The density is also higher than that of pure acid of the same strength, on account of dissolved impurities.

In determining the strength of sulfuric acid by means of hydrometers the above points must be kept in mind, and also the fact that commercial hydrometers are often inaccurate. The Twaddell hydrometer, used in England, has an unaltered scale, each degree corresponding with a difference of density of 0.005. On the Continent and in the United States Baumé's instrument is used, and the degrees of this, according to various authorities, correspond with different densities, so that much confusion has resulted from its use.

The rational Baumé hydrometer is graduated according to the scale:

$$\text{Density (water} = 1 = \frac{144.3}{144.3 - \text{Degrees Bé.}}$$

This scale has been adopted in Germany and France. In the United States the scale:

$$\text{Degrees Bé.} = 145 - \frac{145}{\text{Density}}$$

was formerly adopted, and has been specified by the Bureau of Standards.¹ It is greatly to be regretted that such arbitrary differences should be legalized, and the best course would undoubtedly be to abandon the use of this scale altogether, and work in densities. Tables of comparison of the Baumé and Twaddell degrees and densities are given in Chapter VIII.

The strengths of mixtures of sulfuric acid and water are usually obtained from density tables, those at present most in

1. U. S. Bur. Standards Circular No. 59, 13 (1916); abst. C. A. 1916, 10, 1720.

use being due to Lunge and Isler, Pickering, D. Sidersky,¹ and H. Holler and E. Pfeffer.² Many of the tables are not comparable, as the densities have been taken at different temperatures, or referred to water at different temperatures. Some have been corrected for air-displacement, and others not.³ The Lunge and Isler densities all refer to 15° and water at 4°. They therefore give the weights in grams of 1 cc. acid measured at 15°. The accuracy is given as ± 0.05 .

These tables may be used, of course, only with pure acids, the figures for commercial acids being always higher.

Accurate tables have been prepared by J. Domke and W. Bein,⁴ E. Worden and J. Motion,⁵ W. Ferguson,⁶ and by D. Mendeléeff.⁷

The effect of temperature on the density of sulfuric acid has been given by G. Lunge.⁸ The mean figures are as follows. For each degree C. above or below 15°, add to or subtract from the density observed, the following corrections:

| | |
|-----------------------|--------|
| For acids up to 1.170 | 0.0006 |
| " " from 1.170-1.450 | 0.0007 |
| " " " 1.450-1.580 | 0.0008 |
| " " " 1.580-1.750 | 0.0009 |
| " " " 1.750-1.840 | 0.0010 |

The effect of impurities on the density is variable. The common impurities are lead sulfate, nitrogen oxides and sulfur dioxide. Arsenic and iron usually occur in small amounts only, but Glover acid may be strongly contaminated with these substances, and sodium and aluminium salts may also be present. The effect of sulfur dioxide on the density has been studied by

1. Ann. Chim. anal. 1916, **21**, 197; abst. C. A. 1917, **11**, 320. Chem. Trade J. 1916, **59**, 416.

2. J. A. C. S. 1916, **38**, 1021; abst. C. A. 1916, **10**, 1453; Chem. Zentr. 1916, **87**, II, 640; J. S. C. I. 1916, **35**, 692.

3. G. Lunge and M. Isler, Zts. ang. Chem. 1890, **3**, 129; abst. Jahr. Chem. 1890, **43**, 473; J. C. S. 1891, **60**, 150; J. S. C. I. 1890, **9**, 501. See also G. Lunge and P. Naef, Chem. Ind. 1883, **6**, 37.

4. Zts. anorg. Chem. 1905, **43**, 125; abst. Jahr. Chem. 1905-1908, I, 1572; J. C. S. 1905, **88**, ii, 157.

5. J. S. C. I. 1905, **24**, 178; abst. Jahr. Chem. 1905-1908, I, 1114; J. C. S. 1905, **88**, ii, 280; Chem. Centr. 1905, **76**, I, 1480; Zts. ang. Chem. 1905, **18**, 1773.

6. J. S. C. I. 1905, **24**, 790; abst. J. C. S. 1905, **88**, ii, 632; Chem. Centr. 1905, **86**, II, 1120; Zts. ang. Chem. 1906, **19**, 342.

7. Zts. physik. Chem. 1887, **1**, 273; abst. Jahr. Chem. 1887, **40**, 73; J. C. S. 1888, **54**, 343.

8. "Technical Chemists Handbook," 1910, 126.

J. Dunn.¹ Nitrous acid has a very marked effect on the density of sulfuric acid, although it will probably be in nitrous vitriol only that sufficient oxides of nitrogen occur to interfere appreciably with the densities. A. Marshall² has examined the effects of impurities on the densities of sulfuric acid. Notable amounts of nitric acid may be found in acid recovered from the spent acid of denitrators. An additional 0.1% of various sulfates raises the density of strong acid by 0.001, lead sulfate by 0.0015, arsenous trioxide by 0.0013, nitrosulfonic acid by 0.00027. Lead sulfate is slightly soluble in strong acid: 98% acid may contain 0.09% PbSO₄, and 94% acid, 0.06% PbSO₄.

The effect of arsenous trioxide on the density of sulfuric acid has been observed by R. Kissling,³ and is quite appreciable.

A table prepared by Anthon enables any acid of desired strength to be prepared by mixing *a* parts of C. O. V., 98%, with 100 parts of water at 15° to obtain an acid of density *b*.

The freezing points of sulfuric acid mixed with water have been determined by G. Lunge,⁴ S. Pickering,⁵ J. Thilo,⁶ R. Picquet,⁷ R. Knietsch,⁸ and H. Giran.⁹ The boiling points of the acids have been recorded by G. Lunge.¹⁰

The vapor pressures of sulfuric acid have been determined by V. Regnault,¹¹ by E. Sorel, and by R. Knietsch. The accuracy

1. Chem. News, 1881, **43**, 121; 1882, **45**, 270; abst. Jahr. Chem. 1881, **34**, 162; 1882, **35**, 228; J. C. S. 1882, **42**, 1027.

2. J. S. C. I. 1902, **21**, 1508; abst. Jahr. Chem. 1903, **56**, 348.

3. Chem. Ind. 1886, **9**, 137; abst. Chem. News, 1886, **54**, 96; Ber. 1886, **19**, 668-R; Chem. Tech. Rep. 1886, **25**, I, 163; Jahr. Chem. 1886, **39**, 2047.

4. Ber. 1881, **14**, 2649; abst. J. C. S. 1882, **42**, 362; J. S. C. I. 1882, **1**, 149; Bull. Soc. Chim. 1882, **37**, 497; Chem. Tech. Rep. 1881, **20**, II, 170; Jahr. Chem. 1882, **35**, 101.

5. J. C. S. 1890, **57**, 331; abst. J. S. C. I. 1890, **9**, 290; Bull. Soc. Chim. 1890, **4**, 484; Chem. Centr. 1890, **61**, II, 35; Jahr. Chem. 1890, **43**, 184, 195.

6. Chem. Ztg. 1892, **16**, 1688; abst. J. S. C. I. 1893, **12**, 827; J. C. S. 1893, **64**, ii, 262; Jahr. Chem. 1892, **45**, 325.

7. Compt. rend. 1894, **119**, 642; abst. J. C. S. 1895, **68**, ii, 106; J. S. C. I. 1895, **14**, 35; Chem. Centr. 1894, **65**, II, 961; Jahr. Chem. 1894, **47**, 410.

8. Ber. 1901, **34**, 4100; abst. J. C. S. 1902, **82**, ii, 132; J. S. C. I. 1902, **21**, 172, 343; Jahr. Chem. 1901, **54**, 242.

9. Bull. Soc. Chim. 1913, **13**, 1049; abst. J. S. C. I. 1913, **32**, 788. Compt. rend. 1913, **157**, 375; abst. C. A. 1913, **7**, 3933; Chem. Zentr. 1913, **84**, II, 1196.

10. Ber. 1878, **11**, 370; abst. J. C. S. 1878, **34**, 553; Bull. Soc. Chim. 1878, **30**, 421; Chem. Centr. 1878, **49**, 393; Chem. Tech. Rep. 1878, **17**, I, 454.

11. Ann. Chim. Phys. 1845, (3), **15**, 179; Compt. rend. 1845, **20**, 1127; abst. Pogg. Ann. Phys. 1845, **65**, 135, 321; Ann. Fis. Chim. 1846, **22**, 29, 233.

of the results of the two latter observers have been called in question. Probably the most trustworthy results we possess, apart from those of Regnault, are those of B. Burt.¹

The specific heats of sulfuric acid solutions have been determined by Marignac as follows:

| | |
|---|--------|
| $\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$ | 0.5764 |
| $\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O}$ | 0.7212 |
| $\text{H}_2\text{SO}_4 + 15\text{H}_2\text{O}$ | 0.7919 |
| $\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$ | 0.8537 |
| $\text{H}_2\text{SO}_4 + 50\text{H}_2\text{O}$ | 0.9155 |
| $\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$ | 0.9545 |
| $\text{H}_2\text{SO}_4 + 200\text{H}_2\text{O}$ | 0.9747 |
| $\text{H}_2\text{SO}_4 + 400\text{H}_2\text{O}$ | 0.9878 |

Another table is due to F. Bode.² Knietzsch's figures for oleum³ are very doubtful.

The refractive indices of acids have been determined by V. Veley and J. Manley,⁴ the surface tensions by J. Morgan and C. Davis,⁵ the viscosities by A. Dunstan and R. Wilson,⁶ R. Kremann and R. Ehrlich,⁷ and A. Dunstan,⁸ the free energy of dilution by M. Randall and O. Cushman,⁹ and the reducing effect of free hydrogen by F. Jones.¹⁰

A very important paper on the thermal properties of sulfuric acid and oleum is that of A. Porter.¹¹ In this the author reviews critically the entire subject, and gives a number of tables and curves, some of which are reproduced in Chapter VIII. Since

1. J. C. S. 1904, **85**, 1339; abst. Bull. Soc. Chim. 1905, **34**, 450; Chem. Centr. 1904, **75**, II, 1691; Jahr. Chem. 1904, **57**, 460.

2. Zts. ang. Chem. 1889, **2**, 244; abst. J. S. C. I. 1889, **8**, 543; Ber. 1889, **22**, 419-R; Jahr. Chem. 1889, **42**, 227.

3. Ber. 1901, **34**, 4102; abst. J. C. S. 1902, **82**, ii, 132; J. S. C. I. 1902, **21**, 172, 343; Jahr. Chem. 1901, **54**, 242.

4. Proc. Roy. Soc. 1905, **79**, 469; abst. J. C. S. 1905, **88**, ii, 781; J. S. C. I. 1905, **24**, 1065; Chem. Centr. 1905, **76**, II, 1151; Jahr. Chem. 1905-1908, I, 1574.

5. J. A. C. S. 1916, **38**, 855; abst. J. S. C. I. 1916, **35**, 835; C. A. 1916, **10**, 838; J. C. S. 1916, **110**, ii, 224; Chem. Zentr. 1916, **87**, I, 1119.

6. J. C. S. 1907, **91**, 85; 1908, **93**, 2179; abst. C. A. 1907, **1**, 956; Bull. Soc. Chim. 1907, **2**, 1153; Chem. Zentr. 1907, **78**, I, 1009; 1909, **80**, I, 821; Jahr. Chem. 1905-1908, I, 1573.

7. Monatsh. 1907, **28**, 831; abst. J. C. S. 1907, **92**, ii, 747; Chem. Zentr. 1907, **78**, II, 1290; Jahr. Chem. 1905-1908, I, 80.

8. Proc. Chem. Soc. 1914, **30**, 104; abst. C. A. 1915, **9**, 405.

9. J. A. C. S. 1918, **40**, 393; abst. C. A. 1918, **12**, 549; J. C. S. 1918, **114**, ii, 147.

10. Mem. Manchester Phil. Soc. 1917, **61**, No. 3, 1; J. C. S. 1917, **112**, ii, 530; abst. J. S. C. I. 1917, **36**, 1269.

11. Trans. Faraday Soc. 1917, 241; abst. C. A. 1918, **12**, 517; J. S. C. I. 1918, **37**, 27-A.

these data are intimately involved in the consideration of the concentration of sulfuric acid, they will be deferred until that section (see p. 1352).

Action of Sulfuric Acid on Metals. The action of sulfuric acid of various concentrations and temperatures on different metals is of considerable importance in connection with the manufacture, concentration, storage and utilization of the acid. A considerable amount of meritorious work has been done on this subject, but the results are still largely incomplete, and sometimes contradictory, and this may be due to the circumstance that some metals may assume a passive condition under well defined conditions, and also to the effects produced by traces of impurities in the acid, and more especially in the metal. This is especially the case with lead, as has already been mentioned.

The following general results may be stated: With metals which can decompose water at any temperature (e. g., zinc and iron), dilute sulfuric acid evolves hydrogen. At higher temperatures, the concentrated acid evolves sulfur dioxide from these metals, and zinc may even liberate hydrogen sulfide. Most of the heavy metals (e. g., copper and lead) do not act upon dilute sulfuric acid, or on the concentrated acid in the cold. When heated with concentrated acid, they evolve sulfur dioxide. Gold, iridium and rhodium have no effect on sulfuric acid at any temperature. The action on platinum is discussed below.

Action of Sulfuric Acid on Iron and Steel. Concentrated sulfuric acid has but little action on cast iron, whether hot or cold, provided the acid is prevented from absorbing moisture from the air. The diluted acid, of course, attacks cast iron violently. Thus, salt-cake pots are made of cast-iron, and cast-iron vessels are used for parting gold and silver, for storing and pumping the acid, and for nitration. Some varieties of cast iron resist the action of acids better than others. This question is not yet as clearly decided as might be desired, since the nature of the metal is usually referred to its source rather than to its chemical and physical properties.

G. Lunge¹ gives the following results:

- 1. At the ordinary temperature all acids down to 106° Tw.,

1. Chem. Ind. 1886, 9, 74; abst. Ber. 1886, 19, 668-R; Jahr. Chem. 1886, 39, 2050.

in the absence of air, act very little on all varieties of cast iron.

2. At 100° the action is much stronger. It is least in the case of acid of 168° Tw., 1 $\frac{1}{2}$ times stronger with acid of 142° Tw., and 3 times stronger with acid of 106° Tw.

3. At the boiling point of the acids the differences are far more pronounced. Acid of 168° Tw. acts very little even at its boiling point, 295°, both in the pure state and as commercial acid containing a little N₂O₃, or SO₂. But acid of 142° Tw. acts on the average 14 times stronger at its boiling point, 200°, than the same acid at 100°, and 20 times stronger than acid of 168° Tw. At 200° C. commercial acid of 142° Tw. does not act much different from pure acid of the same strength. Hence it is not feasible to concentrate acid of 142° Tw. in iron vessels, but only acids of 168° Tw. and upwards. Acid of 106° Tw. at its boiling point, 147° acts rather less than acid of 142° Tw. at 200°, but still 14 times as much as acid of 168° Tw. at 295°. There is no difference between pure and commercial acid in this case.

4. The differences between the various mixtures of cast iron are of no importance against acid of 168° Tw. in all cases, and against the weaker acids at 20° and 100°. But the latter acids at their boiling points act decidedly less on charcoal-pig and on chilled cast iron than on the other kinds. A difference between hot and cold casting could not be found. The strongest attack took place on Scotch pig, and mixtures containing it.

R. Knietzsch¹ has examined the action of sulfuric acids and oleum on cast iron, mild-steel and puddled iron. He gives tables for the losses per sq. m. per 72 hours at 18°-20° and remarks that, whereas cast iron vessels resist ordinary acid, they cracked with oleum. The effect is apparently due to the penetration of the pores of the metal, and the conversion of the carbon into carbon dioxide. Remarks on the use of cast iron have been made by Föhr² and A. Ricevuto.³

Wrought iron is acted upon much more than cast iron by weaker acids, but at the ordinary temperature it resists the action of strong acid down to 140° Tw., and probably a little below. After absorption of atmospheric moisture, however, the acid

1. Ber. 1901, **34**, 4109; abst. J. S. C. I. 1902, **21**, 172; Jahr. Chem. 1901, **54**, 242.

2. Chem. Tech. Centralanz. 1886, 545; abst. Wag. Jahr. 1886, **32**, 295.

3. Chem. Ztg. 1907, **31**, 960; abst. Chem. Zentr. 1907, **78**, 11, 1558.

strongly attacks wrought iron (Lunge), the latter being somewhat strongly acted upon by fuming acid containing up to 27% SO_3 (Knietseh). This corresponds with the electrical conductivity of the acid. Towards 27% oleum, wrought iron is quite passive, and resists the acid for years.

The action of sulfuric acid on iron and steel has been studied by C. Fawsitt and C. Powell,¹ with the following results:

1. Concentrated sulfuric acid acts at the ordinary temperature on steel and some kinds of cast iron, with production of ferrous sulfate, hydrogen and a small quantity of sulfur dioxide.

2. The reaction proceeds more rapidly with rise of temperature, and the gaseous products at 180° being sulfur dioxide with occasional small quantities of hydrogen sulfide, but no hydrogen.

3. The rate is increased on the average about 3 times for each 10° rise in temperature.

4. The rate of reaction depends on the concentration of the acid, but for small dilutions the ratio H_2 , SO_2 in the gases remains almost unchanged.

5. Although the rate of reaction depends to a certain extent on the composition of the sample of iron, the nature of the surface is an important factor.

6. The results were the same on the small as on the large scale.

7. It is possible to calculate the conditions of safe carriage of acid.

The effect of arsenic on the action of sulfuric acid on iron has been studied by W. Wiard,² who finds that when the concentration of arsenic in acid of 60°-66° Bé. reaches about 0.003% the rate of action is reduced to about one-fifth. The influence of various substances on the rate of corrosion of iron by sulfuric acid has been investigated by O. Watts,³ but he used weak acid (10%-19%), so that the results are of little interest in the present discussion.

The action of sulfuric acid on various alloys of iron has recently been specially studied. Alloys of iron and silicon occur under various trade names. Tantiron, narki, ironac, elianite, dur-

1. J. S. C. I. 1914, **33**, 234; see also C. Fawsitt and A. Pain, J. Proc. Roy. Soc. N. S. Wales, 1919, **52**, 396; abst. C. A. 1919, **13**, 1799.

2. Chem. Analyst, 1918, **25**, 10; abst. C. A. 1918, **12**, 2184.

3. Paper No. 23, General Meeting Amer. Electrochem. Soc. 1912.

iron, metillür are all varieties of silicon-iron. The great drawback to all these materials is their great brittleness; they are also liable to contain flaws and segregations, so that their manufacture requires much more extensive improvement than has yet been found possible. The acid-resisting properties of all these alloys are similar. The action of dilute sulfuric acid on alloys of iron with vanadium, chromium, tungsten, nickel, cobalt and manganese, has been investigated by L. Aitchison.¹ A. Olle² found that sulfuric acid (sp. gr. 1.180) attacked the glass of the carboy and dissolved iron from it. This is of interest, since acid used for accumulators must be quite free from iron. Pure acid may become contaminated with iron by standing in green glass vessels. Probably lead-lined tanks would be the best receptacles for accumulator acid. The action of sulfuric acid on concrete has been investigated.³

Action of Sulfuric Acid on Lead is a subject of importance, and a considerable amount of work has been done in this field. Some of the results are contradictory, and in many cases they are useless because accurate analyses of the metal were not made. It appears that traces of impurities may have a marked action, so that rough experiments made on metals of unknown composition are without value. Much of the so-called "practical" work is of this type, and is quite useless. Earlier work was carried out by R. Calvert and C. Johnson,⁴ Mallard,⁵ A. Bauer and P. v. Mertens,⁶ J. Glover,⁷ N. Cookson,⁸ J. Mactear,⁹ J. Hochstetter,¹⁰ J. Napier,¹¹ and V. Veley.¹² An extensive series of experiments on the subject has been made by G. Lunge and E

1. J. C. S. 1916, **109**, 288; abst. C. A. 1916, **10**, 1494.
2. Austral. Pharm. Notes, Sept. 1, 1917; abst. C. A. 1918, **12**, 1911 J. S. C. I. 1918, **37**, 112-A.
3. Anon., Dingl. Poly. 1908, **323**, 494; abst. C. A. 1909, **3**, 479.
4. Compt. rend. 1863, **56**, 140; abst. J. C. S. 1863, **16**, 66; Rep. Chim Appl. 1863, **5**, 91.
5. Bull. Soc. Chim. 1874, **22**, 114; abst. Ber. 1874, **7**, 1446.
6. Ber. 1875, **8**, 210; abst. Bull. Soc. Chim. 1875, **23**, 432; Chem. Tech. Rep. 1875, **14**, I, 168.
7. Chem. News, 1882, **45**, 105; abst. Jahr. Chem. 1882, **35**, 1383; Ber. 1882, **15**, 927.
8. Chem. News, 1882, **45**, 105; abst. Chem. Tech. Rep. 1882, **21**, II, 18.
9. Chem. News, 1880, **41**, 236; abst. Jahr. Chem. 1880, **33**, 327.
10. Bull. Soc. Ind. du Nord, 1890, 231; abst. Chem. Tech. Rep. 189 **20**, II, 86; Chem. Ztg. Rep. 1891, **15**, 36.
11. Chem. News, 1880, **42**, 314; abst. Jahr. Chem. 1880, **33**, 328; Chem. Tech. Rep. 1881, **20**, II, 98.
12. J. S. C. I. 1891, **10**, 211; abst. J. C. S. 1891, **60**, 525; 1892, **62**, 41 Ber. 1891, **24**, 522-R, 523-R.

Schmidt.¹ These experimenters found the following results:

1. At higher temperatures the purest lead in all cases resists both pure and nitrous sulfuric acid, with or without access of air, much better than "regulus metal" ($2\text{Pb} + 18\text{Sb}$), or even soft lead with only 0.2% Sb. In the cold, lead with 0.2% Sb is but slightly better than the purest lead; regulus metal is inferior, and hard lead more so.

2. Concentrated nitrous vitriol is always more active than pure acid. In the case of somewhat dilute acid (sp. gr. 1.72 to 1.76) nitrous vitriol acts less than pure acid on soft lead and hard lead, owing to the formation of a protective coating of lead sulfate. With more dilute acid, the action is stronger. In all cases nitrous vitriol acts more in presence than in absence of air.

3. Of two samples of soft lead, the purer one was decidedly better. The presence of only 0.044% of bismuth acts injuriously.

4. It is erroneous to judge the resistance of lead to sulfuric acid by the amount of gas evolved. Soft lead gives off at the ordinary temperature, after a week's contact much more gas than hard lead. Thus, if acid is to be kept in sealed vessels, these should be of hard lead.

5. Lead containing up to 0.2% of copper (alloys containing more copper cannot be homogeneously rolled) is in the cold more strongly acted upon by concentrated sulfuric acid than pure lead; with nitrous vitriol there is not much difference. At 100° all strengths of acid act in the same way on pure lead and on lead containing copper, concentrated pure acid rather less than concentrated nitrous vitriol, but more than nitrous vitriol of sp. gr. 1.72. At 200° C. concentrated acid acts alike on pure lead and on lead containing 0.2% Cu; lead containing more Cu is slightly less acted upon by pure acid, but rather more by nitrous vitriol.

6. Above 200° (225°-255°) lead alloyed with 1% of antimony is far more strongly acted upon than pure lead; but lead containing 0.2% Cu resists the acid at 235° much better than pure lead, and still better at 255°.

7. Pure soft lead gives no visible evolution of gas with pure concentrated acid up to 220°. From this point more gas bubbles are continually given off, and at 260° the lead is instantly dis-

1. Zts. ang. Chem. 1892, **5**, 642; abst. Ber. 1893, **26**, 141-R; Chem. Tech. Rep. 1892, **31**, II, 105; Jahr. Chem. 1892, **45**, 2667.

solved ("flash-point") with strong frothing, smell of SO_2 , and precipitation of sulfur, the temperature rising to 275° .

8. The same lead, alloyed with 0.2% Cu shows a visible evolution of gas only at 260° , regularly increasing up to the boiling point (310°), at which the lead is very gradually dissolved.

9. Soft lead alloyed with 1% Sb gives with sulfuric acid the first visible gas at 175° , more strongly at 225° , and between 275° and 280° there forms a turbulent solution.

Lunge's conclusions are as follows: For chambers, towers, tanks, pipes, and all other instances where the temperature can rise only moderately, and certainly never up to 200° , the purest soft lead is preferable. For very high temperature, e. g., evaporating pans, the addition of 0.1% to 0.2% of copper is advantageous. In the presence of bismuth it preserves the lead from rapid solution. Technical monohydrate, and fuming acid, act much more energetically on lead than the ordinary acid. Concentrated mixtures of sulfuric and nitric acids act very little on lead. The action of nitrous vitriol on lead is least at the point where the nitrosyl-sulfuric acid is still capable of existing, i. e., between sp. gr. 1.5 and 1.6. Bismuth is very injurious to the acid-resisting qualities of lead. The question of the relative superiorities of lead desilvered by the Pattinson or Parkes process, is disputed, the former being usually preferred.

Fluorides, which sometimes occur in blende, cause great wear and tear of lead in the Glover tower and chambers.¹

Action of Sulfuric Acid on Platinum. The action of sulfuric acid on platinum has been investigated by C. Marie,² L. McCay,³ W. Heraeus,⁴ Scheurer-Kestner,⁵ M. Delepine,⁶ and J. Conroy.⁷ The results are more or less contradictory. Conroy's conclusions are as follows:

1. Sulfuric acid, even when pure, exerts a marked solvent

1. Prost, Chem. Ztg. 1902, **26**, 12; abst. J. S. C. I. 1902, **21**, 250.

2. Compt. rend. 1907, **145**, 117; 1908, **146**, 475; abst. Jahr. Chem. 1905-1908, I, 3257; Chem. Zentr. 1907, **78**, II, 1395; 1908, **79**, I, 1373.

3. Eighth Intl. Cong. Appl. Chem. 1912, **1**, 351; abst. C. A. 1912, **6**, 3242; J. S. C. I. 1912, **31**, 928.

4. Chem. Ztg. Rep. 1891, **15**, 36; J. S. C. I. 1891, **10**, 460, 773; Jahr. Chem. 1891, **44**, 2612; 1892, **45**, 2644.

5. Compt. rend. 1875, **81**, 892; abst. Dingl. Poly. 1876, **221**, 82.

6. Compt. rend. 1906, **142**, 631, 1013; abst. Chem. Centr. 1906, **77**, I, 328, 534; Bull. Soc. Chim. 1906, **35**, 10.

7. J. S. C. I. 1903, **22**, 465; J. Soc. Dyers Col. 1903, **19**, 201; abst. Jahr. Chem. 1903, **56**, 714.

action on platinum. The action tends to slow down to a limiting value. The quantity of Pt taken up, 3000 grains per ton, exceeds that found in practice.

2. Above 92% the concentration of the acid has little effect on the action.

3. The rate of action is much influenced by temperature; below 200° it is barely measurable; at 250° it is pronounced.

4. The rate of solution is influenced by certain impurities, but not by others. It is uninfluenced by $(\text{NH}_4)_2\text{SO}_4$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, NaCl , NaNO_3 , but is accelerated by Na_3AsO_3 and PtCl_4 . It is retarded by C, As_2O_3 , S, SO_2 and possibly by N_2O_3 , i. e., by reducing agents.

The Analysis of Sulfuric Acid. In connection with the analysis of sulfuric acid, the following points have to be considered:

1. The gravimetric estimation of sulfuric acid and sulfates.
2. The volumetric estimation of sulfuric acid and sulfates.
3. The analysis of oleum.
4. The analysis of sulfurous acid and sulfites.
5. The qualitative detection of impurities in sulfuric acid.
6. The quantitative estimation of impurities in sulfuric acid.

Some general observations on these topics have already been made; in what follows the different matters will be considered in greater detail.

Gravimetric Estimation of Sulfuric Acid. Sulfuric acid and sulfates are detected in qualitative analysis by the formation of a precipitate of barium sulfate when barium chloride or nitrate solution is added to the solution acidified by hydrochloric or nitric acid. Barium sulfate is practically insoluble in water, dilute acids and solutions of salts. It is slightly soluble in concentrated acids, including sulfuric, especially on heating, and also in solutions of ferric chloride. Care should be taken in carrying out the test that an excess of concentrated hydrochloric acid, with barium chloride, or nitric acid, with barium nitrate, is not added, as then the barium chloride or nitrate may be precipitated. These precipitates are crystalline and re-dissolve when the liquid is diluted and warmed.

Free sulfuric acid is detected in the presence of sulfates in several ways. If the substance is extracted with alcohol, only the free acid dissolves, and may be detected in the solution. Also

if the substance is mixed with a little cane sugar and evaporated in a porcelain dish on the water bath, charring occurs if free sulfuric acid is present. This reaction is not conclusive if sulfates of alumina or ferric oxide are present, or in the presence of free hydrochloric or nitric acid, but may be used to detect free sulfuric acid in acetic, phosphoric and tartaric acids.

Insoluble sulfates may be decomposed by fusing with alkali carbonates, treating with water and adding barium chloride and hydrochloric acid to the filtrate. When melted with fusion mixture on charcoal before the blowpipe they form sodium sulfide, which stains silver black when the moistened mass is placed upon it.

The gravimetric estimation of sulfuric acid is nearly always carried out by precipitating and weighing as barium sulfate. The process has already been described in connection with the analysis of pyrites, so that only a few additional details need be given here. The results are not always quite satisfactory. Z. Karaoglanow¹ finds that in dilute solutions the precipitation depends on the concentration of the acid and on the amount of BaCl_2 added. The quantity of BaSO_4 is said to decrease with increase of BaCl_2 . When precipitation is made from a solution containing a relatively large amount of HCl or HNO_3 the results are too high. The presence of KCl makes the results low; with KNO_3 they are too high. K_2SO_4 gives low results, but in presence of HCl they are too high. In dilute solutions K_2SO_4 is quantitatively converted into BaSO_4 . The presence of chlorides of Na , NH_4 , Zn and Mg does not affect the results; FeCl_3 causes low results except in dilute solutions containing HCl . AlCl_3 in presence of HCl does not interfere, but CrCl_3 causes the low results. Errors are less in the determination of Ba than of H_2SO_4 . Other rules are given by E. Pierce.² R. Silberberger³ states that precipitation as strontium sulfate in alcoholic solution gives accurate results. Zinc salts have no influence in this case. If present, the BaSO_4 method gives incorrect results, unless the zinc is first precipitated by adding

1. Zts. anal. Chem. 1917, **56**, 417; abst. C. A. 1918, **12**, 1445; J. S. C. I. 1918, **37**, 168-A. See also G. Meillere, J. pharm. Chim. 1919, **19**, 296; abst. C. A. 1919, **13**, 2651.

2. Met. Chem. Eng. 1916, **15**, 353; Chem. Eng. Manuf. 1916, **24**, 62; abst. C. A. 1916, **10**, 2793. See Ziegler, J. S. C. I. 1882, **1**, 118.

3. Ber. 1903, **36**, 2755; abst. J. S. C. I. 1903, **22**, 1149; Jahr. Chem. 1903, **56**, 348, 349.

ammonia until the liquid just reddens phenolphthalein.¹ Phosphoric acid also causes too high results. T. von Fellenberg² then adds BaCl_2 drop by drop in not too great excess to the boiling solution, which should contain about 0.13 cc. conc. HCl per 100 cc. Mechanical agitation is recommended by L. Ledoux.³

For accurate results, E. Worden and J. Motion⁴ recommend spraying a 5% solution of BaCl_2 with a fine atomizer into the boiling sulfuric acid solution, of not to exceed 5% strength, the amount of BaCl_2 added being but a trifle over that required to precipitate the H_2SO_4 . The solution is boiled for ten minutes after precipitation in order to increase the size of BaSO_4 crystals, allowed to stand until cold on account of the not negligible solubility of BaSO_4 in water, filtered through a Gooch, washed with warm 2% HCl until the filtrate is free from Ba , and gently igniting.

In the precipitation it is desirable to add the solution of barium chloride which is boiling in one beaker, to the solution acidified with hydrochloric acid which is boiling in another beaker. The precipitate is then always granular, settles rapidly, and may be easily filtered and washed.

The Volumetric Estimation of Sulfuric Acid. The volumetric estimation of sulfuric, in the free state, is usually carried out with standard solutions of caustic potash or soda. As indicators, litmus (in boiling solutions), methyl orange or phenolphthalein, may be used. Litmus cannot be used in presence of sulfides nor phenolphthalein in presence of carbonates or ammonia. Methyl orange may be used in cold solutions in all these cases, but is not as sensitive, a small quantity only being used. Oxalic acid cannot be titrated with methyl orange, but may be used as an indicator for titrating ammonia. Nitrous acid completely interferes with the use of methyl orange, notwithstanding the statement of Lunge to the contrary. When nitrites are present it is better to

1. A. Thiel, Zts. anorg. Chem. 1903, **36**, 84; abst. Chem. Centr. 1903, **74**, II, 523; J. S. C. I. 1903, **22**, 1104.

2. Mitt. Lebensmittelunters. Hyg. 1915, **6**, 191; abst. J. C. S. 1916, **110**, ii, 147; J. S. C. I. 1916, **35**, 490.

3. Bull. Soc. Chim. Belg. 1914, **28**, 51; abst. C. A. 1915, **9**, 184. See also L. Winkler, Zts. ang. Chem. 1918, **31**, I, 212; abst. C. A. 1920, **14**, 259. See Exptl. Rep. No. 105, H. M. Factory Gretna, for the determination of sulfuric acid mist. Report 103 on a modified iodine solution for the Reich test. A N/10 solution is made by dissolving 635 gm. iodine in water containing 150–180 gm. NaOH and making up to 50 liters.

4. J. S. C. I. 1905, **24**, 178; abst. Chem. Centr. 1905, **76**, I, 1480.

use alizarin red as indicator. Ferric and aluminium sulfates may be titrated like the free acid, as they are highly hydrolyzed in solution.

The volumetric determination of sulfates is carried out by Vansteenbergh and Bauzil¹ by heating the solution to 60°–70° with excess of sodium carbonate, filtering, acidifying the filtrate with hydrochloric acid and boiling for 1 minute with a measured excess of 1.22% BaCl₂ solution. The precipitate is washed on a filter and the excess of barium in the filtrate precipitated as carbonate by sodium carbonate. The BaCO₃ is collected, washed, and titrated with N10 HCl, using methyl orange as indicator.

The volumetric estimation of sulfuric acid by means of benzidine was proposed by W. Vaubel,² and improved by F. Raschig,³ W. Mueller and K. Dürkes⁴ and C. Friedheim and O. Nydegger.⁵ The mixture is precipitated with a solution of benzidine hydrochloride, the precipitate of benzidine sulfate being titrated with standard alkali. Numerous precautions must be taken, which are described by Raschig.

Y. Nikaido⁶ titrates with standard lead nitrate in alcoholic solution with iodine as indicator. Yellow PbI₂ appears when all the sulfate is precipitated as PbSO₄. H. Richmond and J. Merrey-wether⁷ employ a calorimetric method for the estimation of strong H₂SO₄. An electrometric method for the estimation of traces of free sulfuric acid in presence of sulfates is described by E. Vulquin and M. Entat.⁸ Dilution of the strong acid with water and a hydro-metric test is advocated by A. Pór.⁹ About 100 cc. of acid are

1. Ann. Chim. Analyst, 1918, **23**, 210; abst. J. S. C. I. 1918; **37**, 689-A; C. A. 1919, **13**, 460.

2. Zts. anal. Chem. 1896, **35**, 163; abst. J. C. S. 1896, **70**, ii, 507; J. S. C. I. 1896, **15**, 385; Jahr. Chem. 1896, **49**, 1119.

3. Zts. ang. Chem. 1903, **16**, 617, 818; abst. J. S. C. I. 1903, **22**, 883, 1066; J. C. S. 1903, **84**, ii, 572, 691; Jahr. Chem. 1903, **56**, 350.

4. Zts. anal. Chem. 1903, **42**, 477. Zts. ang. Chem. 1903, **16**, 653; abst. J. S. C. I. 1903, **22**, 925, 1104; Jahr. Chem. 1903, **56**, 349.

5. Zts. ang. Chem. 1907, **20**, 19; abst. C. A. 1907, **1**, 701; J. C. S. 1907, **92**, ii, 196; J. S. C. I. 1907, **26**, 116; Bull. Soc. Chim. 1907, **2**, 307; Chem. Zentr. 1907, **78**, I, 504; Jahr. Chem. 1905–1908, I, 1588; Zts. anal. Chem. 1908, **47**, 507; 1910, **49**, 464.

6. J. A. C. S. 1902, **24**, 774; abst. J. S. C. I. 1902, **21**, 1247; J. C. S. 1902, **82**, ii, 692; Chem. Centr. 1902, **73**, 820; Jahr. Chem. 1902, **55**, 357.

7. Analyst, 1917, **42**, 273; abst. C. A. 1917, **11**, 2868; J. C. S. 1917, **112**, ii, 503; J. S. C. I. 1917, **36**, 960.

8. Ann. Chim. Analyst, 1917, **22**, 61; abst. J. S. C. I. 1917, **36**, 545; C. A. 1917, **11**, 1804; J. C. S. 1917, **112**, ii, 268.

9. Metall u. Erz., 1916, **13**, 130; abst. Chem. Zentr., 1916, **87**, I, 903;

diluted with 50 cc. water, cooled, and the density taken. It is more convenient to mix equal weights of acid and water. If the strength of this mixture, found from the tables from its density, is multiplied by 2 this gives the strength of the original acid. This method should be used only for acids stronger than 66° B \acute{e} .

The Analysis of Oleum. Reference has already been made to the analysis of oleum. The following additional points may be noted. Equal weights of oleum and water may be carefully mixed, the mixture cooled, and its density taken with the hydrometer. It is preferable to dilute to about 80% H₂SO₄. There is danger of splashing unless the mixing is done carefully. The rest of the oleum, for equal weights, is then added at once, and the mixed acid added to the rest of the water. The SO₃ content of this acid is then found from the tables, and multiplied by 2. This gives the total SO₃ content of the oleum. Monohydrate contains 81.63% SO₃.

The strength of the oleum may also be determined by dilution of a weighed amount and titration. Sulfur dioxide may be estimated by titration with iodine.

The analysis of oleum has been described by C. Fürstenau,¹ W. Möller,² F. Becker,³ C. Winkler,⁴ O. Clar and J. Gaier,⁵ R. Gaunt, E. Thomas and W. Bloxam,⁶ G. Lunge,⁷ P. Dobriner and W. Schranz,⁸ E. Berl,⁹ P. Gavelle,¹⁰ G. Lunge and H. Rey,¹¹ T. C. A. 1917, **11**, 2868. In this connection compare H. Hager, Chem. Centr. 1882, **53**, 776; abst. J. S. C. I. 1883, **2**, 176.

1. Chem. Ztg. 1880, **4**, 18; abst. J. Pharm. Chim. 1880, **2**, 192; Chem. Ind. 1880, **3**, 30; Dingl. Poly. 1880, **238**, 504; Jahr. Chem. 1880, **33**, 1155; Wag. Jahr. 1880, **26**, 237.

2. Chem. Ztg. 1880, **4**, 569; abst. Jahr. Chem. 1880, **33**, 1288; Wag. Jahr. 1880, **26**, 241.

3. Chem. Ztg. 1880, **4**, 600; abst. Chem. Tech. Rep. 1880, **19**, I, 407; Jahr. Chem. 1880, **33**, 1288.

4. Chem. Ind. 1880, **3**, 194; abst. Dingl. Poly. 1880, **237**, 306; Jahr. Chem. 1880, **33**, 1288; Wag. Jahr. 1880, **26**, 238.

5. Chem. Ind. 1881, **4**, 251; abst. Jahr. Chem. 1882, **35**, 1267; Wag. Jahr. 1881, **27**, 167; Zts. anal. Chem. 1882, **21**, 441.

6. J. S. C. I. 1907, **26**, 1175; abst. Chem. Zentr. 1908, **79**, I, 487.

7. "Technical Chemist's Handbook," 143. See also Zts. ang. Chem. 1895, **8**, 221.

8. Zts. ang. Chem. 1896, **9**, 453; abst. J. C. S. 1896, **70**, ii, 672; J. S. C. I. 1896, **15**, 743; Ber. 1896, **29**, 694-R; Jahr. Chem. 1896, **49**, 2086.

9. Chem. Ztg. 1910, **34**, 428; abst. J. C. S. 1910, **98**, ii, 538; Chem. Zentr. 1910, **81**, I, 2041.

10. Mon. Sci. 1913, **79**, 301; abst. C. A. 1913, **7**, 2527; Chem. Zentr. 1913, **84**, II, 82.

11. Zts. ang. Chem. 1891, **4**, 165, describes a pipette suitable for weighing out fuming sulfuric and other acids.

Brewster,¹ G. Finch,² R. Vernon,³ R. Rosenlecher,⁴ M. Gerstner,⁵ J. Prats,⁶ J. Knorr,⁷ R. Setlik,⁸ R. Parker,⁹ H. Rabe,¹⁰ and H. Howard.¹¹

The acid is first liquefied, if necessary, by warming, and well mixed. A sample is then weighed. This may be carried out in a glass bulb, as described by O. Clar and J. Geier, but is most conveniently done in a Lunge pipette, made entirely of glass. Above the tap is a bulb, rather less than an inch in diameter, and above this a second tap. The lower portion of the pipette is ground into a glass tube closed at the bottom. In the conical part of the pipette is a groove reaching half way down, the corresponding half of the groove being in the outer tube. By turning the pipette in the latter the tube can be made to communicate with the outer air, or the reverse. To fill the pipette, the tap is closed and a partial vacuum created in the bulb by suction at the top and closing the tap. The point of the pipette is then dipped into the acid, and opened. When sufficient acid has entered the cock is closed, the outside of the pipette cleaned, and weighed. The pipette is taken out, rinsed out with water into a beaker, then the acid run slowly from the pipette into the water in the beaker. The pipette is then rinsed down into the beaker. Very strong oleum (over 70% SO₃) is best weighed in glass bulbs, which are broken in water in a stoppered bottle. If the oleum is solid, a few lumps may be weighed and then dissolved in a known weight

1. J. A. C. S. 1907, **29**, 1376; abst. Chem. Zentr. 1908, **79**, I, 887; *Jahr. Chem.* 1905-1908, I, 1582.
2. Zts. ges. Schiess. Spreng. 1910, **5**, 167; abst. J. S. C. I. 1910, **29**, 625; J. C. S. 1911, **100**, ii, 150; Chem. Zentr. 1910, **81**, II, 411.
3. Chem. Ztg. 1910, **34**, 792; abst. J. S. C. I. 1910, **29**, 1007; J. C. S. 1910, **98**, ii, 803; Chem. Zentr. 1910, **81**, II, 1247.
4. Zts. anal. Chem. 1898, **37**, 209; abst. J. C. S. 1898, **74**, ii, 404; J. S. C. I. 1898, **17**, 606; Chem. Centr. 1898, **69**, I, 1306; *Jahr. Chem.* 1898, **51**, 405.
5. Chem. Ztg. 1887, **11**, 3; abst. J. S. C. I. 1887, **6**, 289.
6. Eighth Intl. Cong. Appl. Chem. 1912, **1**, 395; abst. C. A. 1912, **6**, 3242.
7. Chem. Ztg. 1912, **36**, 1262; abst. C. A. 1913, **7**, 950; J. C. S. 1912, **102**, ii, 1209; Chem. Zentr. 1912, **83**, II, 2144.
8. Chem. Ztg. 1889, **13**, 1670; abst. J. C. S. 1890, **58**, 414; J. S. C. I. 1890, **9**, 417; Chem. Tech. Rep. 1889, **28**, II, 208; *Jahr. Chem.* 1889, **42**, 2341.
9. J. S. C. I. 1917, **36**, 692; abst. C. A. 1917, **11**, 3007; J. C. S. 1917, **112**, ii, 420.
10. Chem. Ztg. 1901, **25**, 345; abst. J. C. S. 1901, **80**, ii, 473; J. S. C. I. 1901, **20**, 619; Chem. Centr. 1901, **72**, I, 1175.
11. J. S. C. I. 1910, **29**, 3; abst. C. A. 1910, **4**, 1003; J. C. S. 1910, **98**, ii, 239; Chem. Zentr. 1910, **81**, I, 1452.

of analyzed monohydrate in a well-stoppered bottle.

The solution is then titrated as usual. 1 cc. N/NaOH = 0.40035 gm. SO_3 . If S is the amount of SO_3 in 100 parts found by titration, the amount of free SO_3 is given by: free SO_3 = $S - 4.4445(100 - S)$. Instead of calculation, a table prepared by Knietsch may be used (see Chapter VIII).

The preparation of an acid containing a given percentage of SO_3 from oleum and C. O. V. may be carried out by means of this table. Let x be the weight of C. O. V. to be added to 100 parts of oleum to produce an acid containing a per cent. total SO_3 . Then:

$$x = 100 \frac{b - a}{a - c}$$

where b is the total SO_3 per 100 of oleum, and c that in the C. O. V.

Thus, if the oleum contains 25.5% SO_3 , and the C. O. V. 98.2% H_2SO_4 , what weights must be mixed to produce mixed acid containing 19% SO_3 ?

We have: $a = 85.1$; $b = 86.3$; $c = 98.2 \times \frac{80}{98} = 80.1$.

Thus: $x = 100 \frac{b - a}{a - c} = 100 \frac{86.3 - 85.1}{85.1 - 80.1} = 24$.

Thus, 100 parts of 25.5% oleum must be mixed with 24 parts C. O. V. 98.2% H_2SO_4 to form 124 parts oleum of 19% SO_3 .

The presence of SO_2 in oleum necessitates a correction in the titrations.¹

Setlik, and R. Parker, describe a method for the approximate analysis of oleum, depending on the fact that, whereas monohydrate does not fume in moist air, acid containing free SO_3 emits white fumes. 50 gm. of fuming acid is weighed out to 0.05 gm. into a stoppered test tube. Distilled water is run in slowly from a burette, with frequent shaking, so that the white fumes are completely reabsorbed. The cylinder is then opened, and air blown through a glass tube onto the surface of the acid. While any free SO_3 remains, this will cause fuming, which decreases towards the end of the titration and then suddenly ceases. The operation must be carried out in good light, and the temperature of the acid kept below 45°. If 50 gm. acid require, say, 3.55

1. "Technical Chemist's Handbook," 143. See also Zts. ang. Chem. 1895, 8, 221.

cc. water, the free SO_3 present is $3.55 \times \frac{80}{18} = 15.78$ gm.; hence the acid contains 31.56% SO_3 . The method is said to give results as accurate as those obtained by titration.

Detection and Estimation of Sulfur Dioxide and Sulfites.

Sulfur dioxide is readily detected by the smell, and the peculiar oppressive effect on the lungs by very small quantities of the gas, when other odorous gases are absent. It turns lime water milky like CO_2 , but can be separated from that gas by passing through acid KMnO_4 solution, when SO_2 is absorbed. Gaseous mixtures may be passed through a solution of caustic soda, which is afterwards examined for sulfites, as described below. Acidified KMnO_4 is decolorized, and a solution of I_2 in KI is reduced. Test-papers prepared by soaking paper in a solution obtained by boiling 2 gm. starch with 100 cc. of water and adding 0.2 gm. KIO_3 dissolved in 5 cc. of water are turned blue by SO_2 . Sulfur dioxide is reduced by Zn or Al in acid solution to H_2S , which turns lead acetate paper black. A solution of a sulfite if mixed with sodium bicarbonate just acidified with acetic acid, gives a red color or precipitate when poured into a solution of zinc sulfate containing a little sodium nitroprusside. The reaction is more delicate when a little K_3FeCN_6 is added. Thiosulfates do not give this reaction. If a drop of indigo is added to a solution containing sulfites, and the mixture shaken with powdered zinc, the indigo is bleached, owing to the formation of hydrosulfurous acid, $\text{H}_2\text{S}_2\text{O}_4$.

Free sulfurous acid may be estimated by titration with alkali. If phenolphthalein is used as indicator, the point of neutrality is reached with Na_2SO_3 , so that 1 cc. $N/\text{NaOH} = 0.03203$ gm. SO_2 . With methyl orange, however, the point of neutrality is reached at NaHSO_3 , so that 1 cc. $N/\text{NaOH} = 0.06406$ gm. SO_2 . Litmus cannot be used.¹

The solutions may also be titrated with iodine or permanganate. With decinormal solutions, 1 cc. = 0.003203 gm. SO_2 .

A. Sander² found the results with $N/10$ NaOH and methyl orange agreed with those with iodine, but phenolphthalein gave

1. G. Lange, J. S. C. I. 1883, **2**, 513. R. Thomson, Chem. News, 1883, **47**, 136. C. Blarez, Compt. rend. 1886, **103**, 69; abst. Jahr. Chem. 1886, **39**, 1914.

2. Chem. Ztg. 1914, **38**, 1057; Zts. ang. Chem. 1914, **27**, 194; abst. C. A. 1914, **8**, 2132.

no decisive end-point. The end-point with methyl orange is also not very sharp, so that this observer oxidizes the SO_2 by neutral H_2O_2 and titrates the H_2SO_4 formed.⁶ The SO_2 may also be oxidized by boiling with a dilute solution of HgCl_2 .

In sulfites, the sulfurous acid present as Na_2SO_3 , as well as the semi-free acid as NaHSO_3 , may be estimated as follows: The total SO_2 is found by titrating with I_2 , or KMnO_4 and the bisulfite SO_2 by titrating another sample with NaOH and phenolphthalein: $\text{NaHSO}_3 + \text{NaOH} = \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$. Milbauer¹ states that the KMnO_4 should be in tenfold excess. 1 cc. KMnO_4 should = 1 mgm. SO_2 . 20 vols. per cent. conc. H_2SO_4 are added to the KMnO_4 solution, then the sulfite solution, containing at most 1 mgm. SO_2 per cc., after which the excess of KMnO_4 is titrated with oxalic acid, etc.

E. Kedesdy² also oxidizes the SO_2 with H_2O_2 . The titration is made first with NaOH and methyl orange until a yellow color is obtained. H_2O_2 is then added, which oxidizes the NaHSO_3 into Na_2SO_4 and H_2SO_4 . The titration with alkali is continued until a yellow color is obtained.

In a solution containing free SO_2 and bisulfite, the titration is made with NaOH and methyl orange till the color just changes. Then phenolphthalein is added and titration continued till a red color appears. Each cc. of *N* alkali used in the first titration corresponds with 0.06407 gm. free SO_2 ; each cc. in the second titration corresponds with 0.06407 gm. bisulfite SO_2 , or 0.032035 gm. semi-free SO_2 .

E. Knecht and E. Hibbert³ add excess of *N*/10 bichromate made alkaline with NaOH , then acidify with H_2SO_4 . The excess of CrO_3 is determined by titration with titanous chloride. The results agree with those by the iodine method of W. Giles and A. Shearer.⁴ G. Jamieson⁵ titrates with KIO_3 and HCl in pres-

1. Zts. anal. Chem. 1909, **48**, 17; abst. J. C. S. 1909, **96**, ii, 264; J. S. C. I. 1909, **28**, 163; Chem. Zentr. 1909, **80**, I, 578; Jahr. Chem. 1909, **62**, I, 480.

2. Chem. Ztg. 1914, **38**, 601; abst. C. A. 1914, **8**, 2660; J. C. S. 1914, **106**, ii, 485; J. S. C. I. 1914, **33**, 615; Zts. ang. Chem. 1914, **27**, II, 625.

3. J. Soc. Dyers Col. 1915, **31**, 109; abst. J. S. C. I. 1915, **34**, 1089; J. C. S. 1915, **108**, ii, 792; C. A. 1916, **10**, 322.

4. J. S. C. I. 1884, **3**, 197; 1885, **4**, 303; abst. J. C. S. 1886, **50**, 199; Ber. 1885, **18**, 458, 528; Jahr. Chem. 1884, **37**, 1568.

5. Amer. J. Sci. 1914, **38**, 166; abst. C. A. 1914, **8**, 3279; J. C. S. 1914, **106**, ii, 777; J. S. C. I. 1914, **33**, 917.

ence of a drop of chloroform. The analysis of liquid SO_2 is described by R. Pictet.¹

Detection of Impurities in Sulfuric Acid. The detection in sulfuric acid of a residue on evaporation, ammonium sulfate, iron, lead, chlorides, hydrofluoric acid, SO_2 , nitrogen oxides, nitric acid, and selenium, is carried out by the usual methods.

Gaseous impurities are detected by shaking 2 kgm. of the undiluted acid in a half-filled bottle, and testing the air above the acid (1) with starch-iodate paper, (2) or with starch-iodide paper. Turning blue of the first indicates SO_2 , of the second, nitrogen oxides. Lead is shown by the opacity produced by mixing the acid with five times its volume of pure alcohol; larger amounts are deposited on simple dilution of the acid. Iron is detected by boiling with a drop of pure nitric acid, diluting, and adding potassium ferrocyanide, which gives a blue color. F. Venable² finds that the blue color of a mixture of cobalt nitrate and conc. HCl is turned green by traces of ferric salts, but not by ferrous salts. E. Kauder³ states that sulfuric acid containing iron dissolves codeine with a blue color. HF is detected by the etching of a glass plate. Chlorides are detected in the diluted acid by giving a white precipitate with AgNO_3 . Ammonia is detected by diluting 2 gm. of acid with 30 cc. water, adding 4 gm. KOH , and 15 drops Nessler reagent. A yellow or brown color indicates NH_3 . Oxygen compounds of nitrogen are revealed by pouring a strong solution of ferrous sulfate on the acid in a tube, when a red or brown color is produced.⁴ Brucine⁵ gives a red color with nitric acid (not with nitrogen oxides) if excess of H_2SO_4 is present. Nitrous acid may be detected by *m*-phenylenediamine, or sulfanilic acid and α -naphthylamine in the usual way. Arsenic⁶ is shown by the well known Reinsch, Marsh

1. F. P. 435763, Cie. ind. de proc. R. Pictet; abst. J. S. C. I. 1912, **31**, 412.

2. Zts. anal. Chem. 1889, **28**, 699; J. anal. Chem. 1888, **1**, 312; abst. Chem. News, 1888, **58**, 178; Jahr. Chem. 1888, **41**, 2548.

3. Pharm. J. Trans. (3), **18**, 250; abst. Jahr. Chem. 1887, **40**, 2185.

4. G. Lunge, Zts. ang. Chem. 1894, **7**, 345. See also J. Tillmans and W. Sutthoff, Zts. anal. Chem. 1911, **50**, 473. D. de Jong, Pharm. Weekblad, 1913, **50**, 992; abst. Chem. Zentr. 1913, **84**, II, 1824. W. Withers and B. Ray, J. A. C. S. 1911, **33**, 708.

5. G. Lunge and A. Levoff, Zts. ang. Chem. 1894, **7**, 347; abst. J. C. S. 1894, **66**, ii, 398; J. S. C. I. 1895, **14**, 67; Ber. 1894, **27**, 605-R; Jahr. Chem. 1894, **47**, 2446.

6. F. Selmi, Gazz. Chim. Ital. 1880, **10**, 40; abst. Jahr. Chem. 1880,

or Gutzeit tests, applied as elsewhere described herein.

Selenium is often present in sulfuric acid, being contained in some varieties of pyrites. It imparts a red color to a solution of FeSO_4 , SO_2 ,¹ $\text{Na}_2\text{S}_2\text{O}_4$,² or acetylene. A green color is given by codeine salts,³ while aspidospermine⁴ on heating gives a violet color.⁵ Selenium interferes with the detection of arsenic by the Marsh test,⁶ no AsH_3 being given off until all Se has been precipitated.

On the permanganate method, see also N. Busvold,⁷ F. Raschig,⁸ G. Lunge and E. Berl,⁹ L. Winkler,¹⁰ E. Rupp,¹¹ and B. 33, 257. E. Seybel and H. Wikander, Chem. Ztg. 1902, **26**, 50. Arsenic Committee, Soc. Chem. Ind.; J. S. C. I. 1902, **21**, 94. W. Kirkby, Pharm. J. 1901, **66**, 80; abst. J. S. C. I. 1901, **20**, 281. C. Tyrer, Chem. and Drug, 1901, **58**, 389; abst. J. S. C. I. 1901, **20**, 281. E. Dowzard, J. S. C. I. 1900, **19**, 1145. O. Hehner, J. S. C. I. 1901, **20**, 194. F. Bird, J. S. C. I. 1901, **20**, 390. F. Richardson, J. S. C. I. 1902, **21**, 902. A. Gotthelf, J. S. C. I. 1903, **22**, 191. R. Messel, J. S. C. I. 1901, **20**, 192. T. Thorpe, J. S. C. I. 1903, **22**, 974; abst. J. S. C. I. 1903, **22**, 965. G. Bertrand, Bull. Soc. Chim. (3), 1902, **27**, 851; abst. Chem. News, 1902, **86**, 191. C. Parsons and M. Stewart, J. A. C. S. 1902, **24**, 1005. A. Allen, J. S. C. I. 1901, **20**, 281. Manchester Brewer's Assn., J. S. C. I. 1901, **20**, 646.

1. N. Orlow, Chem. Ztg. 1901, **25**, 66; abst. Chem. Centr. 1901, **72**, I, 480; Jahr. Chem. 1901, **54**, 244.
2. J. Meyer and J. Jannek, Zts. anal. Chem. 1913, **52**, 534; abst. C. A. 1914, **8**, 887; J. C. S. 1913, **104**, ii, 788; J. S. C. I. 1913, **32**, 825.
3. E. Schmidt, Arch. Pharm. 1914, **252**, 161; abst. J. S. C. I. 1914, **33**, 748; J. C. S. 1914, **106**, ii, 672; C. A. 1914, **8**, 2990.
4. A. Jouve, Bull. Soc. Chim. 1901, **25**, 489; abst. Chem. Centr. 1901, **72**, I, 1389.
5. L. Palet, Ann. Chim. Analyt. 1918, **23**, 25; abst. J. S. C. I. 1918, **37**, 147-A; C. A. 1918, **12**, 1028.
6. J. M. Meunier, Compt. rend. 1916, **163**, 332; abst. J. S. C. I. 1916, **35**, 1132. L. Dawydow, Farmazef, 1895, 1; abst. Chem. Ztg. Rep. 1895, **19**, 70; Chem. Centr. 1895, **66**, I, 811. O. Rosenheim, Chem. News, 1901, **83**, 277; abst. Chem. Centr. 1901, **72**, II, 231. A. Berry, J. S. C. I. 1901, **20**, 322. J. Schindelmeyer, Zts. öffentl. Chem. 1902, **8**, 3061; abst. Chem. Centr. 1902, **73**, II, 960. See also W. Alexandrow, Zts. anal. Chem. 1909, **48**, 31; abst. J. S. C. I. 1909, **28**, 138. O. Billeter and B. Wavre, Helvetica Chim. Acta, 1918, **1**, 174; abst. J. S. C. I. 1918, **37**, 503-A. W. Firman and A. Cocksedge, E. P. 52, 1909. G. Jamieson, Amer. J. Sci. 1915, **39**, 639; abst. J. S. C. I. 1915, **34**, 713. R. Michael, Chem. Ztg. 1910, **34**, 1210; abst. J. S. C. I. 1910, **29**, 374. H. Steenberge, Chem. Weekblad, 1917, **14**, 647; abst. J. S. C. I. 1917, **36**, 2866. J. Tillmans, Zts. anal. Chem. 1917, **56**, 509; abst. J. S. C. I. 1918, **37**, 163-A; C. A. 1918, **12**, 1865. Anon., Chem. Ztg. 1917, **41**, 132; abst. C. A. 1917, **11**, 2867.
7. Chem. Ztg. 1915, **39**, 214; abst. C. A. 1915, **9**, 1725; J. S. C. I. 1915, **34**, 489.
8. Zts. ang. Chem. 1905, **18**, 1286. Ber. 1905, **38**, 3911. See also J. Rosenheimer and F. Heim, Ber. 1905, **38**, 3834.
9. Zts. ang. Chem. 1906, **19**, 809; abst. Chem. Centr. 1906, **77**, II, 386; J. S. C. I. 1906, **25**, 533.
10. Chem. Zentr. 1915, **86**, I, 503.
11. Zts. anal. Chem. 1906, **45**, 687; abst. Chem. Centr. 1906, **77**, II, 1660; J. S. C. I. 1906, **25**, 1070.

S. Davisson.¹ Lunge's method, carried out as above, is perfectly satisfactory, and the complicated modifications proposed are quite unnecessary. H. Corvazier's method,² by the electrical conductivity, is no improvement on the old method.

The estimation of arsenic, iron and mercury in sulfuric acid is described by H. Nisjenson.³ Selenium may be estimated by the methods described by J. Meyer and W. von Garn,⁴ in which the color of iodine liberated from excess of KI is matched with standards: $\text{SeO}_2 + 4\text{HI} = 2\text{I}_2 + 2\text{H}_2\text{O} + \text{Se}$.

Lunge estimates arsenic by diluting a measured volume of acid, reducing with SO_2 , and titrating in NaHCO_3 solution with iodine. A more exact process is to oxidize precipitated As_2S_3 to As_2O_5 , precipitate Ag_3AsO_4 , and determine the Ag volumetrically, but the simpler process is usually sufficiently accurate.⁵

Hydrochloric acid is estimated by boiling 10 cc. of the acid in a flask, and conducting the vapors over the surface of a little water in a second flask. This absorbs HCl, which is estimated by titration with AgNO_3 .

Hydrofluoric acid is estimated by R. Ehrenfeld⁶ by precipitating the barium salts, and treating with a measured volume of calcium dichromate, in excess, in HCl solution. BaF_2 is converted into chromate, while BaSO_4 is unchanged. The excess of dichromate is titrated back. A simpler method is to allow a bundle of previously weighed glass rods to stand in the acid in a lead beaker for some time. The loss of weight of the rods is compared with that in pure acid with known amounts of HF added.

Impurities in Commercial Sulfuric Acid. Commercial sulfuric acid prepared by the chamber process contains a number of impurities, derived from the pyrites, niter, water, and lead of the chambers, the lining of the Glover tower, etc. In most cases the

1. J. A. C. S. 1916, **38**, 1683; abst. C. A. 1916, **10**, 2448; Chem. Zentr. 1916, **87**, II, 1072.

2. Mon. Sci. 1912, **76**, 322; abst. C. A. 1913, **7**, 1338; J. C. S. 1912, **102**, ii, 1092.

3. Chem. Ztg. 1914, **38**, 1097; Pharm. J. Nov. 14, 1914; abst. J. S. C. I. 1914, **33**, 1080.

4. Zts. anal. Chem. 1914, **53**, 29; abst. J. C. S. 1914, **106**, ii, 67; Chem. Zentr. 1914, **85**, I, 185.

5. J. Pergrin, Ann. Chim. Analyt. 1917, **22**, 24; abst. J. S. C. I. 1917, **36**, 325. R. Tarbell, J. Ind. Eng. Chem. 1914, **6**, 400; abst. J. S. C. I. 1914, **33**, 590.

6. Chem. Ztg. 1905, **29**, 440; abst. J. C. S. 1905, **88**, ii, 417; Jahr. Chem. 1905-1908, I, 1447.

acid is concentrated and used without purification, although for the purposes of making food, chemicals, etc., a pure acid is required. Although contact acid might be expected to be pure, since the burner gas is purified, this is not necessarily the case, since the sulfur trioxide is often condensed in chamber acid, with its impurities.

The impurities of chamber acid which may be present are: arsenous acid, arsenic acid, antimony oxide, selenium (usually as SeO_2), salts of lead, iron, zinc, copper, mercury, calcium, aluminium, and alkalis; sulfur dioxide, nitric acid, nitrous acid (as nitrosylsulfuric acid), nitric oxide (in presence of FeSO_4), hydrofluoric acid and fluorides, and organic matter.

Most of these substances occur in too small quantities to be detrimental, and also do not usually interfere with the common uses of the acid. Thus lead is almost entirely precipitated as PbSO_4 on diluting the acid, and iron separates as ferric sulfate during the concentration. Aluminium sulfate may also be deposited as $\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 14\text{H}_2\text{O}$.¹ Some of the impurities, however, may lead to trouble. Minute amounts of mercury decrease the suitability for pickling brass objects;² iron and platinum (from concentrating stills) make acid unsuitable for accumulators; selenium, petroleum refining,³ and the parting of gold and silver.⁴ Arsenic is nearly always present, and most objectionable. Sulfuric acid is largely used in the manufacture of glucose from starch, and poisoning epidemics have been caused by the use of arsenical acid.⁵

Slight amounts of suspended matter in the acid, usually lead sulfate and charred organic matter, are not objectionable, and are difficult to remove. They are best permitted to subside by allowing the acid to flow slowly through lead tanks. The acid is also usually colored brown from a trace of organic matter.

Estimation of Acidity in Flue and Exit Gases. The estimation of SO_2 and SO_3 in flue gases has been described by R. Nestell

1. A. Hoffmann, *Metall u. Erz.* 1915, **12**, 290, 310; abst. *Chem. Ztg.* Rep. 1915, **39**, 443; *J. S. C. I.* 1916, **35**, 358.

2. B. Deutecom, *Chem. Ztg.* 1892, **16**, 574.

3. F. Schultz, *Chem. Ztg.* 1911, **35**, 1109. For the removal of selenium, see H. Koch, D. R. P. 167457; abst. *Wag. Jahr.* 1906, **52**, I, 527.

4. E. Sorel, "Fabrication de la acide sulfurique," 414. T. Drinkwater, *Analyst*, 1883, **8**, 63; abst. *Ber.* 1883, **16**, 1359; 1884, **17**, 5-R.

5. A. Colombano, *Giorn. farm. chim.* 1913, **62**, 57; abst. *C. A.* 1913, **7**, 3395; *Chem. Zentr.* 1913, **84**, I, 1219.

and E. Anderson,¹ M. Bodenstein and W. Pohl,² J. Kastle and J. MacHargue,³ and H. Rabe.⁴ The acidity of exit gases has been measured by H. J. Watson.⁵ J. Peregrin⁶ describes a self-registering apparatus for determining the oxygen in chamber exit gases.

De-arsenication of Sulfuric Acid. Arsenic is not a normal constituent, in more than traces, of genuine brimstone acid, or that made from most kinds of blende. Acid made from pyrites, however, is practically always arsenical, although in different degrees.⁷ The highest proportion of arsenic occurs in the Glover acid, mainly as arsenious acid; Gay-Lussac acid contains a larger proportion as arsenic acid, due to the oxidizing action of the nitrogen oxides.

PERCENTAGES OF ARSENIC COMPOUNDS IN SULFURIC ACID (HJELT)

(Acids prepared from Spanish Pyrites containing 0.91% As)

| | |
|---------------------------|---|
| Chamber acid..... | 0.202 As of which 0.040 exists as As_2O_3 |
| Glover acid..... | 0.331 As of which 0.041 exists as As_2O_3 |
| Gay-Lussac acid..... | 0.341 As of which 0.132 exists as As_2O_3 |
| Acid of last chamber..... | 0.019 As. |

A large proportion of the arsenic may be condensed from the burner gases in good dust chambers before entering the Glover tower; the rest is mostly collected as mud in the Glover tower by its scrubbing action on the burner gas.

De-arsenicated acid is necessary in the preparation of foods, in cleaning sheets of iron for tinning,⁸ the preparation of pharmaceuticals and of certain dyes, in the Deacon chlorine process, and in making white ammonium sulfate.

Attempts have been made to remove the arsenic from the

1. J. Ind. Eng. Chem. 1916, **8**, 258; abst. J. S. C. I. 1916, **35**, 474; C. A. 1916, **10**, 1017.
2. Zts. Elektrochem. 1905, **11**, 378; abst. J. C. S. 1905, **88**, ii, 581; J. S. C. I. 1905, **24**, 729.
3. Amer. Chem. J. 1907, **38**, 465; abst. C. A. 1907, **1**, 2988; J. C. S. 1907, **86**, ii, 861.
4. Chem. Ztg. 1901, **25**, 345; abst. Chem. Centr. 1901, **72**, I, 1175.
5. J. S. C. I. 1903, **22**, 1279; abst. Chem. Centr. 1904, **75**, I, 764; Zts. ang. Chem. 1904, **17**, 687.
6. Ann. Chim. Analyt. 1916, **21**, 223; abst. J. S. C. I. 1916, **35**, 1216; C. A. 1917, **11**, 387.
7. K. Stahl, Zts. ang. Chem. 1893, **6**, 54. Bräuning, Preuss. Zts. Berg. Hütten u. Salinenwesen, 1877, 142. E. Hjelt, Dingl. Poly. 1877, **226**, 174. See also J. S. C. I. 1901, **20**, 188. G. Davis, Chem. News, 1878, **37**, 155. J. S. C. I. 1883, **2**, 157. E. Filhol and Lacassin, Union Pharm. **3**, 114; abst. Wag. Jahr. 1862, **8**, 212; Rep. Chim. Appl. 1862, **4**, 222.
8. Gossage, Hofmann's Report by the Juries, for the Exhibition of 1862, 12. F. Falding, J. S. C. I. 1906, **25**, 403.

burner gas before entry to the chamber¹ where it is mostly removed from the acid. The purified acid² is sufficiently arsenic-free for all practical purposes. If pyrites containing a large amount of arsenic are used, the entire plant becomes contaminated with arsenic.³ The Gräflich von Landsberg-Velen und Gemensche Chemische Fabrik⁴ oxidizes the As_2O_3 in the gases to non-volatile As_2O_5 , which is removed by washing with acid before entering the chambers. Dust is removed from the gas by filters.

The following methods have been used for de-arsenication of sulfuric acid: distillation; crystallization of the acid by cooling; conversion of As_2O_3 into AsCl_3 and volatilizing or dissolving out the latter; formation of a soap by shaking with colza oil and precipitation of As_2S_3 . The latter method is more commonly used.

The distillation of the acid⁵ will completely remove only As_2O_5 , As_2O_3 passing over with the acid. As_2O_3 may be oxidized to As_2O_5 with a little HNO_3 , and distillation then gives an acid As-free. MnO_2 or a little KMnO_4 (excess is explosive) may be used.⁶ F. Maxwell Lyte⁷ treats the acid with $1/2\%$ – $1/4\%$ oxalic acid to destroy nitrogen compounds, heats to 110° , and after cooling to 100° adds powdered $\text{K}_2\text{Cr}_2\text{O}_7$ in slight excess, a pure acid being obtained by distillation. These processes are too expensive to be used on a large scale.

M. Morance⁸ cools the Glover acid to -8° to $+2^\circ$ for 24

1. F. Girod, E. P. 17157, 1911; abst. C. A. 1913, **7**, 403; J. S. C. I. 1912, **31**, 687; Chem. Ztg. Rep. 1912, **36**, 570. I. Löhme, U. S. P. 1103522, 1914. Can. P. 176011, 1917; abst. C. A. 1914, **8**, 3102; Zts. ang. Chem. 1916, **29**, I, 116; Chem. Ztg. Rep. 1915, **39**, 114; Mon. Sci. 1914, **81**, 178.

2. Bloxam, Pharm. J. (2), **3**, 606. See also Towers, J. S. C. I. 1904, **23**, 221.

3. W. Hardwick, J. S. C. I. 1904, **23**, 218. See also H. Bornträger, D. R. P. 15757; abst. Wag. Jahr. 1881, **27**, 162.

4. D. R. P. 252273; abst. C. A. 1913, **7**, 538; Zts. ang. Chem. 1912, **25**, 2608; Chem. Zentr. 1912, **83**, II, 1587; Chem. Ztg. Rep. 1912, **36**, 620; Wag. Jahr. 1912, **58**, II, 71. D. R. P. 256234; abst. C. A. 1913, **7**, 1944; Chem. Zentr. 1913, **84**, I, 868; Chem. Ztg. Rep. 1913, **37**, 108. D. R. P. 256237, 1910; abst. C. A. 1913, **7**, 1959; Zts. ang. Chem. 1913, **26**, 185; Chem. Zentr. 1913, **84**, I, 756; Wag. Jahr. 1913, **59**, I, 375; F. P. 432874. Aust. P. 60964. Belg. P. 237786, 1911.

5. M. Bussy and H. Buignet, J. Pharm. Chim. 1863, **44**, 177; Ann. 1864, **130**, 249; abst. Wag. Jahr. 1862, **10**, 159; Chem. News, 1864, **9**, 73; J. prakt. Chem. 1864, **92**, 444; Poly. Centr. 1864, **30**, 752.

6. N. Blondlot, Compt. rend. 1864, **58**, 76; abst. Jahr. Chem. 1864, **17**, 144; Chem. News, 1864, **9**, 225.

7. Chem. News, 1864, **9**, 172; abst. Jahr. Chem. 1864, **17**, 145; Chem. Centr. 1864, **35**, 688.

8. Compt. rend. 1909, **148**, 842; abst. C. A. 1909, **3**, 1914; J. S. C. I. 1909, **28**, 520.

hours, removes the crystals of monohydrate, and separates the mother liquor centrifugally. The melted crystals are not arsenic-free, but contain much less than the original acid.

Shaking the acid with 4 or 5 cc. of colza oil per liter, allowing to stand 12 hours, pouring into water, and separating the sticky mud from the purified acid, has been described¹ as a method of de-arsenication.

The two processes exclusively used are the removal as AsCl_3 , and, more commonly, the precipitation as As_2S_3 .²

Separation of Arsenic as Trichloride. AsCl_3 boils at 125° , and can therefore easily be separated from sulfuric acid by heating. If the As_2O_3 in the acid can be converted into AsCl_3 , its separation by this method will be possible. As_2O_3 in presence of conc. H_2SO_4 is easily converted into AsCl_3 by treatment with HCl or chlorides, such as common salt, but the reaction is reversible, and in presence of water, or when the acid is diluted, the AsCl_3 is decomposed again: $\text{As}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons 2\text{AsCl}_3 + 3\text{H}_2\text{O}$. The acid may be heated with common salt,³ or barium chloride;⁴ or a current of HCl gas may be passed into the boiling acid.⁵ The acid may also be heated with 1% NaCl and $1/4\%$ charcoal dust to reduce As_2O_5 , which does not form AsCl_3 .⁶ If a current of HCl is used, heating to 130° – 140° is sufficient, while with NaCl the temperature must be raised to 180° – 190° .⁷ The acid may be diluted with half its volume of water and distilled with PbCl_2 , when AsCl_3 passes off;⁸ chloroform can be added, but this may cause explosions.⁹ The acid is carefully decanted from the

1. See also M. Kugel, *Elektrotechn. Zts.* 1892, **13**, 20; abst. Chem. Ztg. Rep. 1892, **16**, 163.

2. P. Parrish, *J. Gas Lighting*, 1916, **134**, 134; abst. J. S. C. I. 1916, **35**, 535.

3. J. Löwe, *Jahr. physik. Verein Frankfurt a/M.* 1852–1853; abst. *Dingl. Poly.* 1854, **132**, 205.

4. N. Gräber, *Poly. Notizbl.* 1860, **15**, 79; abst. *Dingl. Poly.* 1860, **155**, 230; *Poly. Centr.* 1860, **26**, 412; *Wag. Jahr.* 1860, **6**, 174.

5. A. Buchner, *Buchner's Rep.* 1864, **13**, 23; abst. *Chem. Centr.* 1864, **35**, 600; *Bayer. Kunst. u. Gewerbebl.* 1864, 480; *Poly. Notizbl.* 1864, **19**, 104; *Wag. Jahr.* 1864, **10**, 161.

6. H. Schwarz, *Breslauer Gewerbebl.* 1865, No. 7; abst. *Dingl. Poly.* 1865, **176**, 232; *Wag. Jahr.* 1865, **11**, 232.

7. W. Tod, *Arch. Pharm.* (2), **37**, 269; abst. *Jahr. Chem.* 1856, **9**, 292.

8. F. Selmi, *Ber.* 1880, **13**, 206; abst. *Chem. Tech. Rep.* 1879, **12**, II, 232; 1880, **13**, I, 348; *Jahr. Chem.* 1880, **33**, 257.

9. H. Hager, *Pharm. Ztg.* 1888, **33**, 473; abst. *Chem. Ztg. Rep.* 1888, **12**, 234; *Jahr. Chem.* 1888, **41**, 475.

lead sulfate present, and then distilled at normal pressure.

In 1905 a number of patents were issued on behalf of the United Alkali Co., in England, in which the chloride method is described. In the first patents¹ As is to be separated as AsCl_3 , and the latter treated for commercial use. The acid is subjected in a suitably packed tower to the action of dry HCl gas at a temperature of about 100° preferably as it leaves the Glover tower. Liquid hydrochloric acid, or a chloride, may also be used. A current of air is passed through the mixture.

In another patent² As_2O_3 is to be reduced by charcoal. This is stated³ to be a slow process, and action soon ceases when Se is deposited on the charcoal. This may be overcome by treating with HCl and charcoal or sulfur at 100° or below. If there is still precipitation of Se, this is removed by washing with HCl , with an oxidizing agent such as hypochlorite or chlorate, when charcoal, not sulfur, must be used. The AsCl_3 obtained may⁴ be mixed with just sufficient water to precipitate the Se, which is filtered off; a larger amount of water is then added to precipitate As_2O_3 . In another process⁵ sufficient HCl is added to convert the As into chloride, viz., 3 HCl to each AsCl_3 , and 5 HCl to each AsCl_5 , with an excess for working losses. Under such conditions AsCl_5 is said to escape as a gas, while AsCl_3 is removed by blowing air through the acid. (It is very improbable that AsCl_5 could be formed in this way.) Arsenic and selenium are removed⁶ by mixing cold sulfuric acid of 140°Tw. to 135°Tw. with a little cold HCl of 30%-32% strength, and bringing in contact with finely divided sulfur for about 2 hours. AsCl_5 (?) is reduced to AsCl_3 , which is removed by blowing a current of air through the liquid. The process may be worked continuously by passing the

1. E. P. 7916, 16929, 16930, 16931, 17886, 17887, 1905; abst. J. S. C. I. 1906, **25**, 477, 535; Chem. Ztg. Rep. 1906, **30**, 296, 470; Mon. Sci. 1908, **69**, 108. U. S. P. 848288, 863940; abst. J. S. C. I. 1906, **25**, 477. Belg. P. 190652, 1906. E. P. 126714; abst. J. S. C. I. 1919, **38**, 395-A.

2. E. P. 5151, 1906; abst. C. A. 1907, **1**, 1789; Chem. Ztg. Rep. 1907, **31**, 371; J. S. C. I. 1906, **25**, 318; Mon. Sci. 1910, **73**, 29.

3. E. P. 23130, 1906; abst. C. A. 1907, **1**, 2520; J. S. C. I. 1907, **26**, 823.

4. F. P. 363947; abst. C. A. 1907, **1**, 2325; Mon. Sci. 1907, **67**, 92. See v. Gothard, Chem. Ztg. 1892, **16**, 163.

5. E. P. 30196, 1909; abst. C. A. 1911, **5**, 2706; J. S. C. I. 1910, **29**, 1376.

6. H. Crowther, F. Leach and W. Gidden, E. P. 20509, 1907; abst. J. S. C. I. 1908, **27**, 1018; Chem. Ztg. Rep. 1909, **33**, 186; Mon. Sci. 1912, **77**, 81.

mixture of H_2SO_4 and HCl down a tower packed with S, a current of air being blown through; SO_2 may be employed instead of S by mixing a little with the air blowing through. The air and HCl passing out is first passed into conc. HCl to deposit S and Se, and then into water to decompose AsCl_3 into conc. HCl to precipitate As_2O_3 .

The Verein Chemischer Fabriken, Mannheim¹ remove the AsCl_3 by washing with hydrocarbons, fatty oils, etc., in which it is soluble. Mineral oils are most suitable; brown coal-tar oil may be used but easily decomposable aliphatic glycerides are unsuitable. The gas is washed in a tower or other apparatus with a fine spray of oil, filtered through coke, and preferably dried before being treated with oil. The latter is freed from AsCl_3 for further use by washing with water containing lime, which is subsequently acidified with HCl . The acid is treated with HCl to convert As_2O_3 into AsCl_3 .

The Chemische Fabrik Griesheim Elektron² convert the As into AsCl_3 or AsF_3 and remove these by treatment with benzene or its derivatives, such as dichlorobenzene, or aliphatic compounds, such as carbon tetrachloride. For liquids, CCl_4 is most suitable; for gases, dichlorobenzene or acetylene tetrachloride is preferred. From these solvents the AsCl_3 is eliminated by washing with water. It is applicable only to acids stronger than 58°Bé. , such as Glover acid; weaker acid, as chamber acid, may be treated³ by adding, as well as HCl , a little HI or I_2 , and treating with SO_2 , the iodine being regenerated. By means of a small amount of iodine it is stated that up to 80% of the As may be removed from chamber acid.

Removal of Arsenic as Sulfide. The most common method is to eliminate As by precipitation as As_2S_3 , which is then removed by filtration. This has the advantage that it removes, besides

1. E. P. 16910, 1906; abst. J. S. C. I. 1907, **26**, 760. D. R. P. 179513; abst. Zts. ang. Chem. 1907, **20**, 1068; Chem. Zentr. 1907, **78**, I, 1081; Jahr. Chem. 1905-1908, I, 1469, 1890; Chem. Ztg. Rep. 1907, **30**, 21; Wag. Jahr. 1907, **53**, I, 382; Mon. Sci. 1909, **71**, 65.

2. E. P. 974, 1907; abst. J. S. C. I. 1907, **26**, 1091. E. P. 3435, 1907; abst. J. S. C. I. 1907, **26**, 1238. D. R. P. 194864, 195578; abst. Zts. ang. Chem. 1908, **71**, 791, 1756; Chem. Zentr. 1908, **79**, I, 909, 1218; Jahr. Chem. 1905-1908, I, 1890; Wag. Jahr. 1908, **54**, I, 374, 375; Chem. Ztg. Rep. 1908, **32**, 200; Mon. Sci. 1910, **73**, 145. Aust. P. 32449, 34022. Belg. P. 19/391, 198423. F. P. 376934. Ital. P. 245/84, 246/85.

3. E. P. 3435, 1907; abst. J. S. C. I. 1907, **26**, 1238.

As, several other impurities, such as lead, antimony, selenium, sulfur dioxide, nitrous and nitric acids. The precipitation must be carried out in moderately dilute acid, not above 106° Tw., or at least not stronger than chamber acid. If As_2O_6 is present, the precipitation is slow, as this compound must first be reduced to As_2O_3 .

At first the H_2S required for precipitation was generated in the acid itself by the addition of BaS ,¹ FeS , Na_2S , CaS (alkali-waste), NH_4HS ,² $\text{Na}_2\text{S}_2\text{O}_3$ or BaS_2O_3 ,³ but none of these processes are now in use. The present methods always employ gaseous H_2S , generated in a separate apparatus, as first suggested by W. Hunt.⁴

Three types of apparatus are in use:⁵ (1) The older apparatus, consisting of lead-lined towers,⁶ 5 ft. 4 in. by 5 ft. 6³/₈ in. section, and 16 ft. 3 in. high, in which an ascending stream of H_2S gas meets a descending stream of acid. (2) Closed agitators ("Trepex" type), in which the acid is agitated by paddles and intimate contact with the gas ensured. (3) Intermittent apparatus in which the gas is brought in contact with the acid under pressure. The latest process consists in removing the As_2S_3 by flotation, a hydrocarbon oil being added.

In the design of a de-arsenication plant the following points are of importance:

1. The general plant lay-out should be such as to allow raw acids and sludges to flow from one stage of the process to the other by gravity. Good ventilation must be provided.

2. The H_2S generating plant should be situated away from buildings in which heat is used. The type of apparatus used

1. A. Du Pasquier, *Mem. Acad. Sci.* 1845, **1**, 315; *J. prakt. Chem.* 1846, **38**, 325; *J. Pharm.* 1846, **9**, 415. See Hofmann's Report by the Juries, Exhibition, 1862, 12.

2. G. Thomson and W. Kemp, *U. S. P.* 314548, 1885; *E. P.* 6215, 1884; *abst. J. S. C. I.* 1885, **4**, 212.

3. W. Thorn, *Dingl. Poly.* 1875, **217**, 495; *abst. Chem. Tech. Rep.* 1875, **14**, I, 219.

4. E. P. 1919, 1853. Cf. W. Knocke, *Dingl. Poly.* 1859, **154**, 185; *abst. Wag. Jahr.* 1859, **5**, 145; *Jahr. Chem.* 1859, **12**, 714.

5. H. Cory, *Chem. Trade J.* 1918, **62**, 89; *abst. C. A.* 1918, **12**, 1108; *J. S. C. I.* 1918, **37**, 122-A. See also T. Moore, *J. S. C. I.* 1919, **38**, 399-T; *abst. C. A.* 1920, **14**, 597.

6. F. Bode, *Dingl. Poly.* 1874, **213**, 25; *abst. Wag. Jahr.* 1874, **20**, 259; *Jahr. Chem.* 1874, **27**, 1105.

for this purpose will be subsequently described in detail.

3. Storage room for acids should be ample, and spare parts kept on hand.

4. Means of chemical control must be provided and the raw acids frequently tested. The treated acid is tested by a Marsh apparatus, and gauges used to regulate the constancy of flow of the H_2S gas.

5. The arsenical residues are treated in a plant situated below the filters and settlers in the de-arsenication plant, the filters being of two types. The porous filters consist of slabs of unglazed earthenware, operated by suction. Pebble filters consist of several layers of graduated materials such as gravel, quartz and sand, the total depth of the beds being 9 in. Four to six layers, varying from $\frac{3}{4}$ in. to 3 in. make up a filter. The finest material is placed on the top, and the lowest medium supported on flat bricks, $\frac{1}{4}$ to $\frac{1}{2}$ in. apart, which in turn, are carried on bricks well spaced.

6. The mud should be washed as free as possible from acid. It is worked up in shallow lead pans, heated from below, and agitated. Wet residues are kept continually moving to avoid hardening and sticking to the bottoms. The acid is run off from the pans and sent back to the filters while the mud shrinks in bulk, and is removed.

Early types of de-arsenicating apparatus are described by H. Deacon,¹ D. McKechnie and W. Gentles,² J. Meikle,³ W. Whitehead and G. Gelstharp,⁴ and J. Riley and J. Barnes.⁵

The American method is described by F. Falding.⁶ I. McCay⁷ conducts the operation at 100° under pressure. I. Kupfferschläger⁸ dilutes the acid with its own volume of water, reduces with SO_2 , and treats with H_2S .

A special apparatus for de-arsenicating sulfuric acid has been

1. E. P. 1682, 1871.

2. E. P. 3229, 1877; abst. Chem. Ind. 1878, **1**, 221.

3. E. P. 11866, 1884; abst. J. S. C. I. 1885, **6**, 345.

4. E. P. 18940, 1894; abst. Jahr. Chem. 1895, **48**, 625.

5. E. P. 25444, 1901; abst. J. S. C. I. 1902, **21**, 1533; Chem. Ztg. 1903, **27**, 373.

6. Mig. Ind. **8**, 583.

7. Chem. Ztg. 1889, **13**, 725; abst. Chem. Ind. 1889, **12**, 371; Jahr. Chem. 1889, **42**, 2649.

8. Bull. Soc. Chim. 1885, **44**, 353; abst. Jahr. Chem. 1885, **38**, 2062; Mon. Sci. 1889, **34**, 1434.

described by R. Bithell and J. A. Beck.¹ A process for manufacturing arsenic-free acid is described by F. Girod.²

The porous earthenware filters used to separate the precipitated As_2S_3 are made by Mackenzie & McLauchlan,³ Middlesboro, England, and by S. Bornett & Co.,⁴ Cologne.

A full description of the older tower method, which can be used only with weak acids, is given by F. Bode.⁵ The modifications adopted in American practice are described by F. Falding.⁶

Davis's de-arsenicator⁷ is now largely used in English factories, and comprizes a horizontal washer, consisting of several iron rings, enameled inside, in which revolves an enameled shaft provided with agitating blades dipping into the acid. The shaft revolves 40 to 60 times per minute, and the blades dip into the acid to one-quarter of their depth. The apparatus is therefore on the well known principle of the Porion evaporator. The acid flows in the opposite direction to the gas by means of overflows through the single compartments, and issues through a filter. The excess of H_2S is absorbed by soda or milk of lime. These washers purify 200-300 tons of acid a week, leaving only 1 to $1\frac{1}{2}$ parts of As per million of acid, and occupy a floor space of only 7 ft. by 5 ft.

It is said that acid completely freed from arsenic acts more energetically on lead pans.

Chemically Pure Sulfuric Acid. The preparation of pure sulfuric acid is a matter of considerable difficulty.⁸ Colorless acid, free from As and Fe, is obtained by F. Girod⁹ as follows: The burner gases are mechanically purified and, while still hot, passed over nitrous vitriol to which a little HNO_3 has been added.

1. E. P. 1500, 1913; abst. J. S. C. I. 1913, **32**, 1009.
2. E. P. 17157, 1911; abst. J. S. C. I. 1912, **31**, 687. See also Gräfflich von Landsberg-Velen and Gemensche Chem. Fabr. Berg & Hüttenwerke, G. m. b. H., E. P. 432873 and 432874, 1911; abst. J. S. C. I. 1912, **31**, 127.
3. Chem. Trade J. 1908, **42**, 67.
4. Chem. Ztg. 1909, **33**, 119.
5. F. Bode, Dingt. Poly. 1874, **213**, 25; abst. Wag. Jahr. 1874, **20**, 259; Jahr. Chem. 1874, **27**, 1105.
6. Min. Ind. **8**, 583.
7. Met. Chem. Eng. 1914, **12**, 354. E. P. Appl. 8776, 1919; abst. J. S. C. I. 1919, **38**, 273-A. See also H. Crowther, E. P. 20509, 1907; abst. C. A. 1909, **3**, 1330. G. Thomson and W. Kemp, E. P. 6215, 1884; abst. J. S. C. I. 1885, **4**, 212.
8. E. Schütz, Zts. ang. Chem. 1911, **24**, 487; abst. C. A. 1911, **5**, 2308; Chem. Zentr. 1911, **82**, I, 1455.
9. E. P. 17157, 1911; abst. C. A. 1913, **7**, 403; J. S. C. I. 1911, **30**, 687.

This is denitrated in the process, and several towers may be used. The gases are passed through washing towers fed with weak acid in a finely divided condition, and this acid, which becomes contaminated with As, is fed to the last denitrating tower. The gases then pass to the chambers. The filter is packed with heat-resisting stone-like material, the gases passing in a lateral and upward direction. A. Hayes¹ adds sufficient niter to the 152° Tw. acid from the Glover to destroy the greater part of the HCl present, and oxidize As_2O_3 and SO_2 . The nitrous acid formed is destroyed by adding $1/3\%$ ammonium sulfate and a little lead oxide. It has been found necessary to heat nitrous vitriol somewhat strongly with ammonium sulfate to destroy nitrous acid. The mass is allowed to settle, and the clear liquid cooled in lead pans to -18° . The acid $H_2SO_4 \cdot H_2O$ crystallizes out, and the impure mother liquor decanted. The crystals are washed with pure acid, fused in clean lead vessels, and in this condition is nearly pure.

The only method of making pure acid is by fractional distillation, which is a troublesome process. The operation is usually carried out in large glass retorts placed over an open fire, the neck of the retort passing into a receiver. Should bumping occur, it may be reduced by adding bits of scrap platinum, quartz, or hard coke. A slow current of air may also be passed through the acid.

If 1 cwt. of acid is used, 5 to 6 hours heating are required before the acid begins to boil; after 12 hours one-twentieth has distilled off. The receiver is then changed, and after 36 hours, 90% has come over, at which point distillation is stopped.

The pure acid is now usually made by concentrating the weak acid distilling over in the concentration process, in glass or platinum stills.² G. de Briailles³ details the oxidation of liquid SO_2 by electrolytic oxygen. I. Ceruti⁴ describes the manufacture of accumulator acid as follows: The purest chamber acid (55%—

1. *Sill. Am. J. Sci.* 1848, (2), **6**, 113; abst. *Jahr. Chem.* 1847–1848, **1**, 371; *Dingl. Poly.* 1848, **110**, 104; *Chem. Centr.* 1848, **13**, 796. See also R. Tjaden-Mödderman, *Zts. anal. Chem.* 1882, **21**, 218; abst. *Wag. Jahr.* 1882, **24**, 260; *J. S. C. I.* 1882, **1**, 320.

2. E. Schütz, *Zts. ang. Chem.* 1911, **24**, 487; abst. *Chem. Zentr.* 1911, **82**, I, 1455.

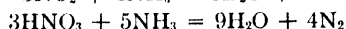
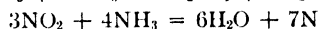
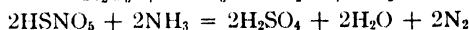
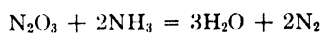
3. E. P. 22434, 1908; abst. *J. S. C. I.* 1909, **28**, 1199.

4. *Ind. Chim.* **10**, 305; abst. *C. A.* 1911, **5**, 1167. See also *Mitt. Lab. Schweiz. Alkoholverwaltung*; abst. *Chem. Ztg.* 1917, **41**, 132; *J. S. C. I.* 1917, **36**, 545.

60% H_2SO_4) is diluted to 40° Bé. with distilled water, and a strong current of air, previously washed with NaOH and H_2SO_4 and heated to 100°, passed through the acid. A fresh clear saturated solution of BaS (2%-3% by vol.) is added. After standing 2 days the acid is decanted and concentrated in silica or lead vessels to 60° Bé.

Purification from Nitrogen Oxides. In purifying sulfuric acid from As by means of H_2S the nitrogen oxides are at the same time removed. If As is not eliminated, it is not customary to remove the small quantities of nitrogen oxides present, unless the acid is to be concentrated in platinum, which is attacked by such acid. Treatment of the acid with SO_2 in pans has been proposed. The Glover tower acid may be completely denitrated, but the iron present in it makes it unsuitable for concentration in platinum. A small preliminary chamber, in which the acid is exposed to fresh burner gas, has also been used. Treatment of the acid with flowers of sulfur, below the melting point, in stoneware boxes placed in the concentrating pans, is a poor method. Löwe heats with oxalic acid, Wackenroder with sugar, W. Skey with charcoal,¹ and Olivier² with alcohol.

The best method is that proposed by J. Pelouze.³ In this the acid is heated with ammonium sulfate, when every trace of nitrogen oxides and acids are removed:



This method is now the only one used. 0.1 to 0.5 lb. ammonium sulfate is sufficient for 100 lbs. of acid. G. Lunge and W. Albenius⁴ find that N_2O_3 is readily destroyed by boiling with ammonium sulfate in the proportion of 1 NH_3 to 1 acid N; even with acid of 140° Tw. this takes place in 5 minutes. But HNO_3 is much more stable; it requires half an hour's boiling with its equivalent of ammonium sulfate, even with the strongest acid.

1. Chem. News, 1866, **14**, 217.

2. Rapports du Jury international, 1867, **7**, 35.

3. Compt. rend. 1841, **12**, 599; Ann. Chim. Phys. 1841, **2**, 47; Ann. 1841, **39**, 312; J. prakt. Chem. 1841, **23**, 499; Ann. Electr. 1841, **7**, 145.

4. Zts. ang. Chem. 1894, **7**, 609; abst. J. S. C. I. 1895, **14**, 35; Ber. 1895, **28**, 11-R; Chem. Centr. 1894, **65**, II, 902; Jahr. Chem. 1894, **47**, 408.

In the case of 140° Tw. acid, several hours' boiling with a large excess of ammonium sulfate are required. C. Kaesmacher¹ passes the acid down a tower against a current of hot air. Dilution and boiling are described by A. Gregoire.²

Decolorizing Sulfuric Acid. Commercial sulfuric acid is often colored brown if it is not stronger than 80%, and acid of about 140° Tw. is usually called "brown oil of vitriol" (B. O. V.) in England. This color may be destroyed during concentration, and also by de-arsenication with H₂S. A red color may be formed from acid of 140° Tw. containing N₂O₃ by contact with iron.³ This is due to NO, formed by reduction, acting on the FeSO₄ formed from the iron. It is destroyed by oxidizing agents. The oleum made by the contact process is colored dark by organic matter, which may be removed⁴ by adding PbO₂ or BaO₂ in the cold, and filtering through sand. A slight yellow color remains with oleum, but C. O. V. becomes water white by this treatment.

Special Methods of Purification. The separation of lead, iron, and arsenic by electrolysis has been proposed. P. Askenasy⁵ subjects the acid to prolonged electrolysis and allows the products to react with the acid. Ozone destroys organic substances and converts HCl into Cl₂; finely divided sulfur reduces nitrogen oxides; H₂S acts in the same way, and also precipitates metals. The electrolysis is carried out at ordinary or slightly elevated temperatures, in vessels without diaphragms, using lead electrodes. The liquid is agitated after the current has acted quietly for some time, the current density being 1-2 amps. per sq. dcm., and the voltage 6. After a few hours the acid is colorless, and may be heated, if necessary, to agglomerate the precipitates.

Hydrofluoric acid may be removed by diluting the acid with

1. E. P. 2382, 1908; abst. J. S. C. I. 1908, **27**, 1019.
2. Bull. Soc. Chim. Belg. 1914, **28**, 32; abst. C. A. 1915, **9**, 184. Cf. also I. Hechenbleikner, Can. P. 191311, 1919; abst. C. A. 1919, **13**, 1905. Exptl. Reports No. 74, 96. H. M. Factory Gretna.
3. R. Nörrenberg, Chem. Ind. 1890, **13**, 363; abst. J. S. C. I. 1890, **9**, 818; Chem. Tech. Rep. 1890, **29**, I, 236.
4. M. Liebig, D. R. P. 164722; abst. Zts. ang. Chem. 1906, **19**, 346; Chem. Centr. 1905, **76**, II, 1473; Jahr. Chem. 1905-1908, I, 1619; Chem. Ztg. 1905, **29**, 1232; Wag. Jahr. 1905, **51**, I, 404; Chem. Zts. 1906, **5**, 77.
5. D. R. P. 86977; abst. Zts. ang. Chem. 1896, **9**, 326; Jahr. Chem. 1897, **50**, 514; Chem. Ztg. 1896, **20**, 503; Wag. Jahr. 1896, **42**, 331; Ber. **29**, 569.

twice its volume of water, and heating for fifteen hours, replacing the water as it evaporates.

Selenium frequently occurs in pyrites and commercial sulfuric acid,¹ and may cause temporary or permanent discoloration. Free Se exists usually in sulfuric acid as a red colloidal material; otherwise the element occurs in the form of SeO_2 . Selenic acid, H_2SeO_4 , is not a normal constituent of chamber acid, since it is only formed by the action of powerful oxidizing agents on Se or SeO_2 . The seleniferous pyrites give SeO_2 on burning, but this is partially or wholly reduced to Se by the SO_2 . The Se is found in the Glover tower as a red sludge, and partly dissolved in the acid, to which it imparts a red color. SeO_2 is also present, usually in greater amount. The red Glover acid is decolorized in the Gay-Lussac tower, since the nitrogen oxides convert Se into SeO_2 . About 20% of the Se in the burner gases is stopped by the Glover tower, the rest passing to the chambers; in the leading chamber as Se, and in later chambers partly as SeO_2 . The back chambers usually contain only SeO_2 .

On concentration, the SeO_2 may be reduced by adding charcoal, but then usually redissolves, forming a green solution of SSeO_3 . When the concentration exceeds 96.5 this again disappears, SeO_2 being formed. The Se may be obtained from the sludge of the Glover tower in the following way. The sludge is agitated with conc. H_2SO_4 and NaNO_3 corresponding with the Se. Water is gradually added, then steam passed in until the density is reduced to 1.26, and the nitrogen oxides eliminated by a current of air. To the filtrate and washings a little HCl is added, and the Se precipitated by SO_2 . It forms a red jelly, which, when washed with water and dried at 105° , contains 99% of Se. This may be estimated in the raw material by digesting on the water bath with conc. HNO_3 , diluting, removing nitrogen oxides by a current of air and titrating with KMnO_4 , which converts SeO_2 into SeO_3 .

The red color due to Se in the acid may be removed by adding HNO_3 , or KMnO_4 .²

Miscellaneous processes for purification of sulfuric acid, or

1. G. Davis, J. S. C. I. 1883, **2**, 157. G. Lunge, Chem. Ind. 1883, **6**, 128. See also S. Littmann, Zts. ang. Chem. 1906, **19**, 1039, 1081; abst. J. S. C. I. 1906, **25**, 693. L. Deutsch, Zts. ang. Chem. 1906, **19**, 1329.
2. G. Le Roy, Mon. Sci. 1901, **57**, 406; abst. Jahr. Chem. 1901, **54**, 243. F. Schulz, Chem. Ztg. 1911, **35**, 1129; abst. C. A. 1912, **6**, 802.

preparation of pure acid, have been described by F. Teed,¹ B. Dirks,² O. Martin and F. Jaeger,³ W. Windus,⁴ W. Hasenbach,⁵ H. Kuehne,⁶ C. Opl and the Erste Oesterr. Fabr.,⁷ the Consortium f. Elektrochem. Ind.,⁸ E. Wenmaekers,⁹ and others.¹⁰

General Methods of Concentration. The sulfuric acid obtained from the chambers, of 106° to 124° Tw., is sufficiently strong to be used for many purposes without further concentration. Thus, it may be employed for the preparation of superphosphates and alum, and even for saltcake, though stronger acid is now always used for the latter. The acid from the Glover tower is of 144° to 152° Tw., and serves for the majority of purposes for which sulfuric acid is used. In some applications of the acid as in the refining of petroleum, however, as strong an acid as possible is required, and the Glover tower acid has then to be concentrated in special apparatus.

A preliminary concentration of chamber acid in lead pans was formerly extensively employed, but since the introduction of the Glover tower this process is no longer necessary. The vapor emitted by boiling weak acid is practically free from acidity, so there is no loss in this stage of the process. Acid up to 144° Tw., or even 152° Tw. acts very little upon lead, while stronger acid may be concentrated in iron.

At first, the acid was concentrated by boiling in small glass retorts. Platinum stills were introduced into English works about 1850, and were for a long time used for the later stages of concen-

1. E. P. 17612, 1887; abst. J. S. C. I. 1888, 7, 846.
2. D. R. P. 295906, 1915; abst. J. S. C. I. 1917, 36, 646; Chem. Zentr. 1917, 83, I, 293; Chem. Ztg. Rep. 1917, 41, 52; Ann. Rep. Soc. Chem. Ind. 1917, 2, 181.
3. U. S. P. 1148522; abst. C. A. 1915, 9, 2488.
4. E. P. 367, 1882; abst. Wag. Jahr. 1883, 29, 265.
5. U. S. P. 838034; abst. C. A. 1907, 1, 476; Mon. Sci. 1907, 67, 113.
6. D. R. P. 203541; abst. Zts. ang. Chem. 1909, 22, 267; Chem. Zentr. 1908, 79, II, 1654; Jahr. Chem. 1905-1908, I, 1609; Wag. Jahr. 1908, 54, I, 373. Aust. P. 40422, 1909.
7. Aust. P. 36098, 36099, 1908.
8. Aust. P. 19708, 1904.
9. Aust. P. 13335, 1903. Belg. P. 155569, 1901.
10. Badische Anilin u. Sodafabrik, D. R. P. 133247. Aust. P. 11301, 1902. See also Aust. P. 1093. Zts. Elektrochem. 1900, 263. Chem. News, 1906, 93, 78. Chem. Fabrik Griesheim-Elektron., Aust. P. 32449, 1907. D. R. P. 179543. U. S. P. 833034. Aust. P. 34022, 1907. Gräflich von Landsberg-Velen und Gemensche Chem. Fabr., Aust. P. 60964, 1913. W. Menzies, E. P. 3230, 1893; abst. J. S. C. I. 1884, 3, 172; D. R. P. 28768; abst. Wag. Jahr. 1884, 38, 299. United Alkali Co., Aust. P. 28436, 1907.

tration. These were repaired by soldering with gold. Iron pans were used for strong acid by Hartmann,¹ who remarks that "iron vessels are not available for evaporating the acid in the state in which it is drawn from the leaden evaporating vessels, as the acid in this state acts upon iron energetically," but could be used for stronger acid. J. Gridley obtained provisional specifications² for this invention. He states that "sulfuric acid of 66° Bé. at 60° F. has little or no action on cast iron, and my invention consists first of the process of introducing a small stream of the dilute acid from the evaporating pans, say of 60° Bé., into a large quantity (say a ton or more) of acid of the strength of 66° Bé. contained in a concentrating pan or retort charged originally with acid of 66° Bé., and kept thereafter at the boiling point. The feed of dilute acid is to be so regulated as not to reduce the acid in the concentrating pan or retort below 65° Bé. at the surface or acid line, at which point, and four inches below the surface, the pan at the sides is protected from the action of the acid. The fact that cast iron resists the action of concentrated acid had, however, been known for many years previously, since pans of the material were used for parting gold and silver by boiling the granulated alloy with sulfuric acid of sp. gr. 1.848.

Improvements in concentrating apparatus have proceeded along the following lines:³ (1) The use of cascades of pans, down which acid flows, the pans and acid being heated by hot air sweeping below them and also over the surface of the acid. (2) The Gaillard tower, in which a spray of acid is sent down an empty tower of volvic lava or acid-resisting material, up which hot gases from a coke producer sweep. (3) The Kessler process, in which hot gases sweep over the surface of the acid flowing through channels in a shallow dish of lava. In the cascade process, the maximum strength of acid produced is 93%. In the Gaillard and Kessler processes, acid of 98%–99% can be produced. Recent processes have been described by O. Kausch.⁴

The efficiency of concentrating apparatus has been discussed

1. E. P. 2839, 1879; abst. J. A. C. S. 1880, **2**, 301.
2. E. P. 4709, 1882; abst. J. S. C. I. 1883, **2**, 281.
3. G. Lüttgen, Chem. Ztg. 1910, **34**, 23; abst. C.-A. 1910, **4**, 1224.
See also F. Meyer, J. S. C. I. 1903, **22**, 781. P. Hart, J. S. C. I. 1884, **3**, 355.
4. Chem. App. 1914, **1**, 272; abst. C. A. 1915, **9**, 955.

by N. Swinden,¹ but all the data in this field has been superseded by the recent paper of A. Porter,² in which the subject is very fully discussed, with numerical examples. This data will be taken as fundamental in the rest of this section.

Theory of the Concentration of Sulfuric Acid. All calculations on the concentration of sulfuric acid were based on more or less uncertain data until the appearance of a recent treatment of the subject by A. Porter, in which all previous data has been critically examined.

Porter represents the heat required to concentrate an acid containing 1 part SO_3 to M_1 parts of H_2O , to one containing 1 part SO_3 to M_2 parts H_2O as follows: $Q = L(M_1 - M_2) + hm_1 - hm_2$. The acid is supposed to be, in the first place, separated completely into SO_3 and H_2O , the heat required for which operation is given by hm_1 . The water is then evaporated to such an extent that just sufficient remains to form the final acid. The heat required will be $L(M_1 - M_2)$, where L is the latent heat of evaporation, at the given temperature, of pure water. The rest of the water, M_2 parts, is then supposed to be mixed with the SO_3 to form the final acid, when heat hm_1 is evolved. The total heat required is then easily seen to be as stated above. It will be noticed that Porter refers all acid strengths to content of SO_3 ; this is a decided advantage since his formulas also apply to oleum, in which case the total SO_3 content must be taken.

After these few remarks, the tables given in Chapter VIII may now be explained. If changes of temperature occur during the evaporation, as is invariably the case in practice, we require also the heat capacities of sulfuric acids of various strengths. These are given in Table XCIV headed Sensible Heat at Constant Concentration. The tables involved in practice are on pages 1539 and 1540, in which all heat quantities are given in C. H. U., i. e., the heat required to raise 1 lb. of water through 1°C. as unit. The weights of acid are in lbs.

Table XCIII gives the Heats of Total Evaporation. By these are meant the quantities of heat, in C. H. U., required to evaporate completely a mixture of 1 lb. SO_3 with the amount of water corresponding to the percentage of total SO_3 given in the first

1. Chem. Trade J. 1916, **59**, 369; abst. C. A. 1917, **11**, 386.

2. Trans. Faraday Soc. 1918, **13**, part 3. See also N. Heinz and J. Geib, U. S. P. 1277922; abst. C. A. 1918, **12**, 2412; J. S. C. I. 1918, **37**, 724-A.

column, and to decompose (theoretically) the vapor into SO_3 and H_2O . The difference between two numbers in the table, at given temperatures, gives the heat required to evaporate an acid containing the first percentage of total SO_3 to an acid containing the second percentage of SO_3 . Thus, suppose we start with chamber acid of 76% H_2SO_4 at 35°C ., and concentrate it at 160° to R. O. V. of 96% H_2SO_4 . How many units of heat will be required per lb. of final acid?

The initial acid contains $76 \times \frac{80}{98} = 62\% \text{ SO}_3$. (This num-

ber, and the % SO_3 corresponding with a given Bé. gravity, may be read off directly from the Table of Densities in Chapter VIII.)

The final acid contains $96 \times \frac{80}{98} = 78.5\% \text{ SO}_3$. The unit weight of acid always taken in the calculations is that containing 1 lb. SO_3 , i. e., $100/78.5 = 1.27$ lb. strong acid. The weak acid is first raised to 160° from its initial temperature of 35° . For this purpose we require sensible heat given by the Table XCIV, viz., 26 C. H. U. The acid is now evaporated from 62% SO_3 to 78.5% SO_3 at 160° , for which purpose we require heat given by Table XCIII, viz., $778 - 511 = 267$ C. H. U. If we recover no heat in cooling the hot concentrated acid, we require, theoretically, $26 + 267 = 293$ C. H. U. per 1.27 lb. strong acid, i. e., 230 C. H. U. per lb. 96% acid. By comparing this with the actual amount of heat required as found from the fuel consumption, the efficiency of the concentration apparatus is found. The amount of cooling water required for cooling the hot concentrated acid from 160° to (say) 20° , is also easily calculated from the Table of Sensible Heats.

The tables also give data for the heat evolved in absorbing SO_3 in oleum, diluting oleum with oil of vitriol, and other calculations. For a simple graphical method of calculation, consult the original paper.

Concentration in Iron Vessels. Cast iron resists the action of sulfuric acid of concentration greater than 93% to 94%. Such a strength is attained by concentration in silica or acid-resisting metal pans in cascades, and the concentration may, and often is, completed by allowing the acid from the cascade to flow through a large cast iron pan heated below by a fire. Acid of 98% may

be obtained in this way, such as is required in petroleum refining, the manufacture of nitroglycerol and pyroxylin. In case the pan is emptied, enough Strong acid should always remain to give at least 96% acid when the pan is filled up with 93% acid for re-starting.

The pan usually employed is provided with a cover in which there are three necks. One of these is used for the feed acid, the other two for carrying away acid vapor. The outlet for concentrated acid is placed near the bottom. If the pans are used to complete cascades, the top of the cover has one outlet for acid vapor, the inlet being a lead tube running through two semi-cylindrical pieces, one in the pan and the other in the cover, at the side. It is stated that each ton of acid concentrated dissolves about 100 gm. iron, and the fuel consumption is 28%-30% of the acid concentrated.¹ From time to time the mud formed, consisting of ferric sulfate, must be removed. G. Lunge² describes several types of iron pots used in America. In some cases round cast iron pans, 3 ft. wide and 2 in. thick, with double flanges for a hydraulic joint for the cover, are used. The cover may be of lead, water cooled. Such pans last about 2 months, and, when used for concentrating acid for petroleum refining, may be heated by heavy petroleum (sp. gr. 0.833), injected by a steam jet. The flame, after heating the pans, may pass under lead pans for preliminary concentration.

A pan designed by W. Quinan is of cast iron, divided into three compartments by longitudinal partitions, leaving openings at alternate ends, so that the acid travels in a zig-zag manner. The pan bottom bulges outwards to correspond with these channels, so as to give a greater heating surface. The flat cover is held in place by six lugs, and is luted on with a mixture of barytes and water glass. The cast iron vapor pipe is fitted on in the same

1. A. Düron, E. P. 2408, 1913; abst. J. S. C. I. 1913, **32**, 791; C. A. 1914, **8**, 2606. D. R. P. 267138; abst. C. A. 1914, **8**, 795; Chem. Zentr. 1913, **34**, II, 2013; Chem. Ztg. Rep. 1913, **37**, 674; Wag. Jahr. 1913, **59**, I, 379. D. R. P. 275751; abst. C. A. 1914, **8**, 3180; Zts. ang. Chem. 1914, **27**, 478; Chem. Ztg. Rep. 1914, **38**, 410; Wag. Jahr. 1914, **60**, I, 166. F. P. 453733, 453742; abst. J. S. C. I. 1913, **32**, 790; C. A. 1913, **7**, 3645; Chem. Ztg. Rep. 1913, **37**, 474. E. P. 3444, 1913; abst. J. S. C. I. 1913, **32**, 911; C. A. 1914, **8**, 2607.

2. Zts. ang. Chem. 1894, **7**, 135. A. Scheurer-Kestner, Bull. Soc. Ind. Mulhouse, 1892, 348. D. R. P. 61331; abst. Bull. Soc. Ind. Mulhouse, 1892, 320; Zts. ang. Chem. 1892, **5**, 213; Wag. Jahr. 1892, **38**, 294; Ber. 1892, **25**, 482.

way. The acid inlet is a cup cast on the pan. Below this the pan bottom is thickened, as this part is most corroded. The pans are 5 ft. 6 in. long, 1 ft. 6 in. broad, and 10 in. deep. The channels are 5 in. wide and the thickness of metal $\frac{5}{8}$ in. The acid outlet is the neck leading to a mud box and rising pipe.

Chilled cast iron is said to be most resisting; the life of a pan is from 4 to 8 months. Small holes may be luted with water glass and asbestos powder, with a little barytes. The deposit of ferric sulfate formed in the pan may be removed once a fortnight. The consumption of fuel is 28% to 30% (used as petroleum).

Arrangements of iron pans have been described by Schuerer-Kestner; in which platinum domes are used. Platinum apparatus has now, however, practically gone out of use.

J. Herreshoff, H. and G. Nichols¹ describe a combination of platinum and iron apparatus, in which the acid is distilled in the iron retorts, yielding very pure acid.

S. Dreyfus and the Clayton Aniline Co.,² use cast iron pans in which acid of any strength, is fed on the center of the surface of heated acid of not less than 90%-93%, at the same time withdrawing strong acid from the bottom of the vessel so that the level remains constant. This is exactly the same arrangement as described by J. Gridley in 1882³ and M. Walsh⁴ in 1884. The pan has an overflow taken from near the bottom of the pan and delivering the acid corresponding with the working level in the pan. The cover is cemented to a flange and carries an inlet pipe, a vapor outlet, and a hole for a thermometer. The pan is charged with 90%-93% acid, which is heated to boiling, and fresh acid is then run in.

C. Krell⁵ uses a cast iron tube heated in a bath of molten lead. This apparatus appears to have been successfully used in

1. E. P. 1998, 1887; abst. J. S. C. I. 1887, **6**, 370. U. S. P. 357528; abst. J. A. C. S. 1886, **8**, 39. Cf. Der Norske Akt. f. Elektrokemisk Ind. and M. Halvorsen, F. P. 363157; abst. J. S. C. I. 1906, **25**, 847; Chem. Zts. 1906, **5**, 328; Mon. Sci. 1907, **67**, 92. E. P. 3680, 1906; abst. J. S. C. I. 1906, **25**, 1146.

2. E. P. 11544, 1898; abst. J. S. C. I. 1899, **13**, 494.

3. U. S. P. 265495; abst. Wag. Jahr. 1883, **29**, 266.

4. U. S. P. 291821, 1884; abst. J. A. C. S. 1884, **6**, 52; Wag. Jahr. 1884, **30**, 299.

5. E. P. 18727, 1894. D. R. P. 166557, 176944. E. P. 4063, 1906. F. P. 363604; abst. Chem. Centr. 1906, **77**, I, 418; J. S. C. I. 1906, **25**, 927. See also M. Liebig, Zts. ang. Chem. 1900, **13**, 184. E. Hartmann and F. Benker, Zts. ang. Chem. 1906, **19**, 565. G. Stolzenwald, Zts. ang. Chem. 1910, **23**, 1977.

Germany and Poland. The consumption of coal is 30% on acid of 97%-98% strength. W. Hartmann¹ states that the addition of iron salts to the acid, which are again separated in the concentration, adds to the life of the pan.

J. Fisher, J. Hall and F. Moore² run the acid through a cast iron pipe, externally heated, to effect continuous concentration. P. Kestner³ uses his well-known vertical tubular concentrator, with iron tubes placed upright, the acid being raised by bubbles of vapor. J. Mackenzie⁴ runs acid of sp. gr. 1.55 from a store tank through a lead coil, heated by waste gases from a tower below, filled with bricks, where it is brought to sp. gr. 1.775 to 1.80 by direct contact with hot fire gases from the iron pot below, in which the final concentration is effected. In this, hot air, produced in a chamber containing cast iron pipes, is blown through, the pot being heated by gases from the air heater. The temperature of the cast iron pot need not exceed 270°, since the hot air blown through the acid assists the elimination of water. H. Ellison⁵ uses a closed pan of cast iron, the acid to be concentrated being introduced through a pipe of resisting material, of rather less diameter than the pan, with a serrated bottom edge. The heat of the surrounding strong acid effects concentration, and the acid emerging into the outer pan is sufficiently concentrated not to attack the metal. Gellen⁶ uses an iron cascade system. A. Proelss and W. Hall⁷ lead the acid to the cast iron pot through a packed extension, and a second pot, where the acid passes over the bottom in a thin layer. H. Friedrich⁸ describes an apparatus similar to that of J. Gridley, while R. Evers⁹ uses two coils of

1. E. P. 2839, 1879; abst. J. A. C. S. 1880, **2**, 301.

2. E. P. 27376, 1898; abst. J. S. C. I. 1899, **18**, 1124.

3. E. P. 21548, 1912; abst. J. S. C. I. 1913, **32**, 409. D. R. P. 121339, 177304; abst. Chem. Ztg. 1901, **25**, 674; Chem. Ztg. Rep. 1906, **30**, 415; Wag. Jahr. 1901, **47**, I, 552; 1906, **52**, I, 571; Chem. Zts. 1902, **1**, 217. E. P. 12502, 1906; abst. J. S. C. I. 1907, **26**, 516.

4. E. P. 26278, 1904; abst. Chem. Trade J. 1905, **36**, 160; J. S. C. I. 1905, **24**, 196.

5. E. P. 17760, 1902; abst. J. S. C. I. 1903, **22**, 950.

6. Aust. P. Ann. 5616.

7. U. S. P. 960702; abst. Chem. Ztg. Rep. 1910, **34**, 342; Mon. Sci. 1910, **73**, 130.

8. Chem. Ztg. 1909, **33**, 478; abst. J. S. C. I. 1909, **28**, 653; Chem. Zentr. 1909, **80**, I, 2030; II, 566; Wag. Jahr. 1909, **55**, I, 342.

9. D. R. P. 176369; abst. Zts. ang. Chem. 1907, **20**, 1066; Chem. Centr. 1906, **77**, II, 1668; Jahr. Chem. 1905-1908, I, 1615; Chem. Ztg. Rep. 1906, **30**, 387; Wag. Jahr. 1906, **52**, I, 391; Mon. Sci. 1908, **63**, 169; Zts. Schiess. Spreng. 1906, **1**, 427.

interposed pipes on the bottom of the pan. L. Stange¹ heats the acid from outside in conical cast iron pans, and blows hot air over the surface. The bottom of the pan is cooled to prevent the sediment burning on. The acid enters through a stoneware vessel inside the pan, with an opening at the bottom, so that the weak acid floats on the surface of the strong acid in the pan.

S. Dreyfus² describes an apparatus of cast iron for obtaining acid of 95% and upwards. He believes that the stronger acid is always at the bottom of the apparatus. The apparatus consists of a cast iron pan overflowing into an external cast iron pan, charged with 90%-93%. The acid to be concentrated is introduced through a pipe, the vapor escaping through another pipe. The apparatus is heated by a grate fire and by hot gases passing through the flues. The acid passes alternately downwards and upwards to the outermost space, and is withdrawn from the bottom of the outer vessel.

A. Düron³ describes a concentrating apparatus, the floor of which is divided into three approximately parallel channels, along which the acid, introduced through a regenerator column, flows in a zig-zag path. Superheated gas passes in the opposite direction along the side channels, and in the central channel is made to pass through the acid, on to which it is conducted in a number of parallel currents at right angles to the direction of flow, by means of a series of blind transverse channels having walls depending into the acid and communicating alternately with each side channel.

J. Leitch⁴ describes a three-stage concentrating apparatus, arranged in a cascade. The acid is fed to the first stage pans, which are of lead, where it is concentrated to 75%-80% at 100°-125°. It then passes to the second stage basins, of silica, glass,

1. E. P. 91, 1907; D. R. P. 188901; U. S. P. 837592; F. P. 373326; abst. J. S. C. I. 1907, **26**, 907; Zts. ang. Chem. 1908, **21**, 796; Chem. Zentr. 1907, **78**, II, 1283; Jahr. Chem. 1905-1908, I, 1616; Wag. Jahr. 1907, **53**, I, 337; Chem. Ztg. Rep. 1907, **31**, 72, 324; Mon. Sci. 1907, **67**, 113; Chem. Zts. 1907, **6**, No. 419.

2. U. S. P. 1217577; E. P. 101641, 1916; Can. P. 175488, 1917; abst. C. A. 1917, **11**, 190, 1526, 2945; J. S. C. I. 1916, **35**, 1155; 1917, **36**, 457.

3. F. P. 453733, 453742, 1913; abst. J. S. C. I. 1913, **32**, 790; C. A. 1913, **7**, 3645; Chem. Ztg. Rep. 1913, **37**, 474.

4. U. S. P. 1257894, 1257895; E. P. 16001; 1915; Swiss P. 74443, 1917; E. P. 1495, 1915; abst. C. A. 1917, **11**, 1526, 2029; 1918, **12**, 980; J. S. C. I. 1916, **35**, 308; 1918, **37**, 242-A.

porcelain, or iron alloy, in which it is concentrated to 85%–90% at 135°–150°. The acid is then passed to cast iron or iron alloy pans, where it is brought to 96%–98% at 200°–215°.

F. Brandenburg¹ uses cylinders of cast iron or quartz, continued below into cones with lateral pieces, heated on the outside. Strong circulation is said to be obtained.

The Galizische Karpathen Petroleum A. G. vorm. Bergheim, Garvey & Gellen² use a cast iron apparatus consisting of a pan, with an outlet for concentrated acid, and heated by a direct fire. This has a cover prolonged into an alembic, all heated outside by fire gases to prevent condensation. There is a set of dishes inside the alembic, the lowest resting on projections attached to the pan sides. The lowest dish has a central opening through which acid runs into the pan below. The weak acid is fed to the top dish, the vapors passing to a recuperator tower, down which weak acid flows.

A combined tower and pan system is described by E. H. Armstrong.³ The acid first passes through a tower for preliminary concentration to 62°–63° Bé., and then through cast iron pans in a furnace; one above the other, the last pan being direct fired, to bring it to 93%–97% H₂SO₄. The furnace gases pass under the pans to the tower, where they mix with the acid vapors from the pans, pass up the tower, and escape through scrubbers.

Ferrosilicon, for concentration apparatus, is described by A. Jouve;⁴ many varieties are now on the market. A new alloy, "illium," chiefly Ni and Cr, is described by S. Parr.⁵

Concentration in Lead Pans. A preliminary concentration of chamber acid in lead pans was formerly extensively used, but since the introduction of the Glover tower has gradually been abandoned. The pans may be heated from the top, by hot gases, from below by waste heat, or by steam. The quality of lead

1. D. R. P. 243544; abst. C. A. 1912, **6**, 2299; Zts. ang. Chem. 1912, **25**, 596; Chem. Zentr. 1912, **83**, I, 695; Chem. Ztg. Rep. 1912, **26**, 156; Wag. Jahr. 1912, **58**, I, 377; Zts. Schiess. Spreng. 1912, **7**, 98.

2. D. R. P. 271625; Aust. P. 60565; abst. C. A. 1914, **8**, 2465; Zts. ang. Chem. 1914, **27**, 252; Chem. Zentr. 1914, **85**, I, 1316; Wag. Jahr. 1914, **60**, I, 296.

3. J. Ind. Eng. Chem. 1917, **9**, 1730.

4. F. P. 330666; abst. J. S. C. I. 1903, **22**, 1086; Chem. Zts. 1903, **2**, 742; Mon. Sci. 1904, **61**, 67.

5. Amer. Inst. Metals, Sept. 1915. U. S. P. 1115239; abst. J. S. C. I. 1914, **33**, 1161; 1915, **34**, 1097.

especially suitable for such pans as have been discussed by W. Hart.¹

Lead pans heated from above have been described by Godin,² G. Junge,³ W. Clough,⁴ C. Grosse-Leege,⁵ A. Bernutat,⁶ F. Girod⁷ and O. Brünler.⁸

Lead pans heated from below are much smaller than the first type, and require careful heating to avoid melting. They are placed on metal plates, which may be covered with a layer of sand. J. MacDougall⁹ supports the pans on perforated iron plates; J. Carulla¹⁰ interposes a thin copper plate between the pan and the iron plate. A number of pans in series are used, the fireplace being usually under the pan containing the weak acid. Six pans, 5 ft. 7 in. long and wide, and 12 to 16 in. deep, make a good combination. A. Junge¹¹ has described the pans used at Freiburg. Other modifications are detailed by The Zeitzer Eisengiesserei,¹² and W. Wolters.¹³

Pans operated by waste heat from other concentration apparatus, or the burners, are used even where there is a Glover tower. Sometimes the Glover tower is used to concentrate the

1. J. S. C. I. 1907, **26**, 504; abst. C. A. 1907, **1**, 2295. Cf. H. Ditz and F. Kannhäuser, Zts. anorg. Chem. 1916, **98**, 128; abst. J. C. S. 1917, **112**, ii, 208; J. S. C. I. 1917, **36**, 641.
2. Ann. des Mines, 1865, 344.
3. Dingl. Poly. 1871, **201**, 341; J. C. S. 1871, **24**, 1100; Chem. Tech. Rep. 1871, **10**, II, 126.
4. U. S. P. 15222, 1856; abst. Rep. Chim. appl. 1860, **2**, 323; 1861, **3**, 48; Jahr. Chem. 1860, **13**, 691; Wag. Jahr. 1860, **6**, 173.
5. D. R. P. 176370; abst. Zts. ang. Chem. 1907, **20**, 893; Chem. Centr. 1906, **77**, II, 1668; Jahr. Chem. 1905-1908, I, 1616; Chem. Ztg. Rep. 1906, **30**, 371; Wag. Jahr. 1906, 52, I, 391; Mon. Sci. 1908, **69**, 169; Zts. Schies. Spreng. 1906, **1**, 427.
6. D. R. P. 281133; abst. Zts. ang. Chem. 1915, **28**, 83; Chem. Zentr. 1915, **86**, I, 176; Chem. Ztg. Rep. 1915, **39**, 11; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111.
7. E. P. 17158, 1911; abst. C. A. 1913, **7**, 403; J. S. C. I. 1912, **31**, 335; Chem. Ztg. Rep. 1912, **36**, 330.
8. D. R. P. 283790, 1913; abst. C. A. 1915, **9**, 2577; Zts. ang. Chem. 1915, **28**, 296; Chem. Zentr. 1915, **86**, I, 1031; Chem. Ztg. Rep. 1915, **39**, 191.
9. E. P. 21778, 1895; abst. J. S. C. I. 1895, **14**, 158. See also Alkali Insp. Rep. **31**, 54.
10. J. S. C. I. 1893, **12**, 15.
11. Jahr. Berg. u. Hüttenw. Sachsen, 1892; abst. Zts. ang. Chem. 1893, **6**, 61; Wag. Jahr. 1893, **39**, 381.
12. D. R. P. 99768; abst. Wag. Jahr. 1898, **44**, 328; Chem. Centr. 1899, **70**, I, 239; Jahr. Chem. 1898, **51**, 1588; Chem. Ztg. 1898, **22**, 1937.
13. E. P. 18831, 1893; abst. J. S. C. I. 1894, **13**, 887. D. R. P. 73689; abst. Wag. Jahr. 1894, **40**, 449; Zts. ang. Chem. 1894, **7**, 175; Ber. 1894, **27**, 429; Mon. Sci. 1894, **44**, 55, 81; J. Organ. Chem. 1894, II, 384.

acid for the Gay-Lussac tower, and the balance of the chamber acid concentrated in lead pans.

Lead pans heated by steam appear to have been proposed by J. Smith and J. Savage,¹ and at the Duisburg works such pans were used,² consisting of wooden tanks lined with lead, containing lead steam coils for steam under 45 lbs. pressure. Apparatus on the principle of the tubular boiler have been advocated by A. Kux,³ H. Egells,⁴ and the International Vacuum-Eismachinen-verein.⁵ Steam pans have also been described by C. Kurtz⁶ and Solvay & Co.⁷

Concentration in Glass Vessels. Concentration by boiling in glass retorts was introduced by Chance Bros., Oldbury, England. The retorts consisted of a large body, blown of thin glass, about 3 ft. high and 1 ft. 9 in. diameter, with a loose head like the beak of a retort, fitting into a lead trunk running along the retort house, and communicating with a chimney. The retorts were heated on flat metal sand baths. The distillation took one day, when the retort was allowed to cool, and the acid drawn off by a siphon. The same process was used at Mühlheim.⁸ A process of continuous working has been introduced by J. Gridley,⁹ in which the retorts were placed terrace-wise in a furnace, and connected by siphons, the acid flowing through the entire series. The retorts were afterwards heated separately by large Bunsen burners. The strength of the acid does not rise above 92% or 93%, and the plant is suitable only for small works. Otherwise it acts efficiently.

Modifications of the apparatus have been described by S. Bowen,¹⁰ G. Veitch,¹¹ R. Penniman¹² and C. Schofield.¹³ Estimates

1. U. S. P. 41647, 1864.
2. R. Hasenclever, Hofmann's Report, 1875, **1**, 185; abst. *Jahr. Chem.* 1875, **23**, 1054.
3. D. R. P. 31277; abst. *Wag. Jahr.* 1885, **31**, 218; E. P. 8803, 1884; abst. *J. S. C. I.* 1885, **4**, 499.
4. D. R. P. 31620; abst. *Wag. Jahr.* 1885, **31**, 219.
5. D. R. P. 37353, 38015; abst. *Wag. Jahr.* 1887, **33**, 508, 509; *Chem. Centr.* 1887, **58**, 472.
6. D. R. P. 38018; abst. *Wag. Jahr.* 1887, **33**, 508.
7. D. R. P. 54730; abst. *Zts. ang. Chem.* 1891, **4**, 89; *Wag. Jahr.* 1891, **37**, 375; *Ber.* 1891, **24**, 423.
8. A. Fehrmann, *Wag. Jahr.* 1886, **32**, 263; *Chem. Tech. Rep.* 1886, **25**, II, 305. *V. Lütj.* *Zts. ang. Chem.* 1892, **5**, 385; abst. *J. S. C. I.* 1893, **12**, 153.
9. E. P. 1243, 1871.
10. E. P. 2035, 1883; abst. *J. S. C. I.* 1884, **3**, 30. See also R. Rap-

of the cost of concentrating in glass retorts have also been given.¹ Detailed description of the process is hardly necessary, as it has been replaced by more efficient modern apparatus.

Concentration in Silica. Quartz was fused into a pasty condition by Gaudin in 1839 by means of the oxy-hydrogen blowpipe, and similar experiments were made by Gautier in 1878. The preparation of filaments of fused quartz was described by Boys, and other experiments were made by Dufur and LeChatelier. In 1901 Shenstone described his work on working quartz before the oxy-hydrogen blowpipe to the Royal Institution in London, and showed how tubes of quartz could be made. In 1903 Dr. Heraeus detailed a similar method of working quartz to the 5th International Congress of Applied Chemistry. Shenstone's methods were adopted by the Silica Syndicate of London, and Heraeus' by his firm at Hanau.

Quartz, or rock crystal, is far too expensive a material for use in making technical apparatus, and heating with oxy-hydrogen blowpipe could be applied to small articles only. The attention of experimenters was therefore directed to the use of sand, and electrical heating. This was first effected by Hutton, in 1902, who described the method to the American Electrochemical Society. Sand or particles of rock crystal were piled round a central core, which was heated electrically, or an arc flame was played over the surface of the granular material. The core was afterwards removed, and a tube remained. Patents were taken out by Elihu Thomson in the United States, and the Ruhstrat firm in Germany for this process, but led to no practical results. The chief difficulties in fusing quartz lie in its high melting point, and the close proximity of the melting and vaporizing points.

Experiments were made at Wallsend, in England, by Bottomley and Paget, in which silica was converted into a plastic, but not fused condition by heating in the electric furnace, and the apparatus made in this way was suitable for use on a technical and F. Leeth, *J. S. C. I.* 1882, **1**, 320.

11. E. P. 7901, 1889; abst. *J. S. C. I.* 1889, **8**, 983.

12. U. S. P. 469439; abst. *J. A. C. S.* 1892, **14**, 41.

13. E. P. 19780, 1891; abst. *Chem. Centr.* 1893, **64**, I, 996; *J. S. C. I.* 1893, **12**, 155.

1. Hofmann's Report, 1875, **1**, 188. *Min. Res. U. S.* 1888, 673. F. Tate, *J. S. C. I.* 1894, **13**, 208, 473. See also *Chem. Trade J.* 1906, **38**, 77. See also T. Webb, D. R. P. 61752; abst. *Wag. Jahr.* 1892, **38**, 292; *Zts. ang. Chem.* 1892, **5**, 278; *Ber.* 1892, **25**, 483.

nical scale. The materials are made by electrically heating a carbon core or plate embedded in sand to a high temperature.

To prevent the pasty silica from sticking to the heater, it is stated that the latter is first wrapped in paper, leaving a thin protecting film of carbon between the heater and the silica. The material is known as Vitreosil, and is made by the Thermal Syndicate at Wallsend, being¹ extremely resistant to mineral and organic acids, with the exception of hydrofluoric acid and phosphoric acid above 400°. It has a low coefficient of expansion, so that it may be heated strongly and cooled by immersion in cold water without breaking. It melts at about 1750°, but begins to soften at 1400°. Owing to crystallization, it cannot be used for prolonged work above 1100°. The chief drawback to the material from the technical point of view is its fragility, although this does not appear markedly in the form of dishes. In the form of spiral tubes the writer has found it extremely fragile, and does not recommend it for such purposes.

Shallow pans of vitreosil, with lips, or rectangular pans with lips, are used for acid concentration, chiefly in the cascade system. The heat transmitting properties of vitreosil have been studied by W. Lewis.² The writer has been informed by a manufacturer that silicon-iron has better heat transmitting properties at lower temperatures than vitreosil, but that the reverse holds above a red heat.

C. Stoffmehl³ concentrates sulfuric acid in a set of silica dishes placed partly inside and partly outside a tower of acid-proof material in such a manner that they are heated consecutively by the fire gases. The dishes placed inside the tower are fed with the acid previously concentrated in the dishes outside the tower, the dishes being arranged in a spiral manner.

Voelcker & Co.⁴ manufacture articles of quartz by fusing

1. U. S. P. 812399, 822424; 1906. U. S. P. Re-13504, 1913. Chem. Trade J. 1911, **48**, 85. Alkali Insp. Rep. 1907, **44**, 28. Pohl, Zts. ang. Chem. 1912, **25**, 1850. See also Chem. Trade J. 1912, **51**, 650. Cf. I. Schlossberg, U. S. P. 1128659, 1915; D. R. P. 258683, 1911; abst. J. S. C. I. 1913, **32**, 605; 1915, **34**, 232.
2. J. Ind. Eng. Chem. 1915, **7**, 410; abst. J. S. C. I. 1915, **34**, 600.
3. F. P. 460627; abst. C. A. 1914, **8**, 2230; Chem. Ztg. Rep. 1914, **38**, 128. Belg. P. 258323, 1913.
4. D. R. P. 258351; abst. C. A. 1913, **7**, 2673; Chem. Zentr. 1913, **84**, 1558. Cf. F. Brandenburg, D. R. P. 243544, 1910; abst. J. S. C. I. 1912, **31**, 334; C. A. 1912, **6**, 2299; Chem. Zentr. 1912, **83**, I, 695; Wag. Jahr. 1912, **58**, I, 377; Chem. Ztg. Rep. 1912, **36**, 156.

sand round an electric resistance core and uniting the quartz body by blowing.

Siloxide is another refractive material¹ stated to have advantages over vitreosil. The Aussiger Verein für Chemische und Metallurgische Fabrikation² manufacture quartz tubes by an arc flame inside the tubes to be made. Silicon nitride is recommended by Herre³ for use in concentrating acids, and silicon tubes are made by the Carborundum Co. at Niagara Falls for carrying hot mineral acids.

An apparatus for concentrating in quartz is described by A. Zanner.⁴ The final stage of the concentration is effected in series of quartz or other trays arranged in a shallow muffle heated as far as possible uniformly by gases from the producer. The trays may be mounted in the muffle or sunk in its floor. The preliminary concentration may be carried out in trays directly exposed to the furnace gases. The draft is regulated by dampers.

W. Hof⁵ distills acids continuously by running them down slightly inclined tubes of quartz which are heated. He states that a ton of acid can be evaporated per 24 hours per sq. m. of tube surface.⁶

Porcelain or Enamel Apparatus. The use of enameled iron instead of cast iron for concentrating pans was proposed by Roder.⁷ A method of coating the inside of an iron pot with iron sulfate, by heating a mixture of sulfuric acid and alkaline pyrosulfate in it was described by W. Wolters.⁸ F. Tate⁹ refers to an enameled apparatus. E. Dyson¹⁰ used a cascade apparatus

1. A. Pohl, Zts. ang. Chem. 1912, **25**, 1849. Zirkonglasges. G. m. b. H., Zts. ang. Chem. 1912, **25**, 2349. See F. Wolf-Burckhardt and W. Borchers, E. P. 18053, 1911; abst. C. A. 1913, **7**, 407; J. S. C. I. 1912, **31**, 189. F. P. 432786; abst. J. S. C. I. 1912, **31**, 130.

2. Aust. P. Ann. 4345.

3. Chem. Ztg. 1914, **38**, 317, 341; abst. C. A. 1914, **8**, 2036.

4. D. R. P. 260555; Belg. P. 155775, 1901; 160924, 1902; 259249, 1913. U. S. P. 693635, 1902; abst. J. S. C. I. 1902, **21**, 476.

5. E. P. 21291, 1913; abst. J. S. C. I. 1914, **33**, 865. D. R. P. 260655, 1912; abst. J. S. C. I. 1913, **32**, 751. F. P. 462016. U. S. P. 1099308; abst. Chem. App. 1919, **6**, 66; C. A. 1919, **13**, 2974.

6. In this connection, see also F. Bottomley, J. S. C. I. 1917, **36**, 577.

7. Dingl. Poly. 1836, **61**, 397.

8. D. R. P. 15639; abst. J. A. C. S. 1882, **4**, 110; Wag. Jahr. 1882, **28**, 264; Mon. Sci. 1882, **24**, 324.

9. J. S. C. I. 1894, **13**, 208; abst. Jahr. Chem. 1894, **47**, 408.

10. E. P. 17699, 1893; 27769, 1896; abst. J. S. C. I. 1894, **13**, 1059; 1897, **16**, 918; Mon. Sci. 1895, **46**, 49. See also Chem. Trade J. **17**, 339.

composed of iron pans lined with special enamel, and connected by U-shaped siphons. This plant was in use in England in 1902. Seckendorff¹ concentrated the acid in flat-bottomed iron retorts completely surrounded by the fire from which the acid was to be distilled. J. Gridley² protects cast iron pans at the top by asbestos cement. C. Flanagan³ uses enameled cast iron pans with water-cooled lead hoods.

The enamel for apparatus of this kind should be of very good quality; the writer has tested dishes from one English firm which were completely resisting to boiling sulfuric acid for a long time, and did not crack when suddenly heated or cooled, so that it is possible to produce a suitable enamel on a commercial scale.

Concentration in Platinum Apparatus. Although formerly platinum stills were largely used for the final concentration of sulfuric acid, the steadily increasing price, and in some cases steadily decreasing quality, of that metal, have led to its abandonment in a great many instances since modern methods, especially the Kessler and Gaillard processes, do not require platinum.

It will therefore be unnecessary to describe the platinum concentration apparatus in detail, but the most important features of the still may be briefly given.

The main source of platinum is the Ural Mountain district in Russia. The production of the metal in troy ounces (1 oz. troy = 31.1035 gm.) for the years 1900-1912 averaged about 300,000. In consequence of internal troubles this large source of supply has for some years been interrupted, and the remaining sources have become of greater interest. These are, in comparison with the Russian mines, quite insignificant. Beds of platinum ore in the United States, especially in California, Oregon, and in Canada, yield less than 1000 troy oz. per annum; new beds have been reported recently in the Yellow-Pine district, Clark County, in Southern Nevada. Australia yields about 300-400 ozs.

Most of the platinum ore is worked up by the firms of John-

1. Hannover Pat. Sept. 7, 1855; abst. Hannov. Mitth. 1855, 306; Wag. Jahr. 1855, **1**, 56.

2. U. S. P. 265495; abst. J. S. C. I. 1883, **2**, 41; Wag. Jahr. 1883, **29**, 266.

3. E. P. 3530, 1901; abst. J. S. C. I. 1901, **20**, 1112.

son & Matthey, in London, and Desmoutis, Lemaire & Co., of Paris.

The modern types of platinum stills are those of Prentice,¹ and G. Delplace.² The former is of an elongated square shape, 3 ft. by 1 ft. 6 in. for 4 or 5 tons O. V. per day. The principal feature of these stills is the corrugated bottom of the pan, which gives a greatly increased heating surface. The thin stratum of acid in the pan at any time, i. e., the use of shallow pans, is another feature of the recent types.

In the Delplace system two stills are used, the top one being fed with acid of 144° Tw. and the distillate, from the still below. The latter carries the concentration up to 98%.

The platinum stills supplied by the firm of Desmoutis, Lemaire & Co. are also of the shallow type, the pan having concentric partitions which cause the acid to traverse the still in a circuitous manner, overflowing from the pipe. They are sometimes made in an elongated shape instead of circular.

The firing of platinum stills is a matter of great importance, the best system of firing being with producer gas. The Liegel producer is specially adapted for this purpose.

Since the pan is the only part of the still coming in contact with the hot acid, Harrison Blair & Co., of Bolton, England, and A. Smith, of Dublin, used lead covers cooled by water. This plan was reintroduced by H. Roessler in 1863, at Griesheim,³ but was abandoned until ten years later, when the firm of Faure & Kessler, of Clermont-Ferrand, introduced an improved type of apparatus, which is generally known by their name. It consists of a platinum dish, with a rim shaped to form a hydraulic lute, which is covered with a lead hood composed of a cylinder surmounted by a cone. This hood is double walled, and is cooled by a current of water. The condensate forming on the inside of the hood runs off through a tube. The cooler for the acid running from the still has been used in connection with other systems, and the writer has been assured that it is very efficient indeed. It consists of a lead vessel with an internal hood connected by three

1. See Anon., *Chem. Ind.* 1878, **1**, 113; 1879, **2**, 109. J. Stroof, *Chem. Ind.* 1878, **1**, 194.

2. D. R. P. 23159, 1882; abst. J. S. C. I. 1884, **3**, 107; *Wag. Jahr.* 1883, **29**, 266.

3. *Dingl. Poly.* 1865, **176**, 34; abst. *Jahr. Chem.* 1865, **18**, 776.

lead tubes with an exterior water vessel. A lead water coil is also placed inside the lead vessel. Vitreosil coolers are also used,¹ but if coils are used, these are exceedingly easily broken, and are not recommended. Most works using silica dishes on cascades for concentration employ lead coolers.

The Faure & Kessler system has not been developed to any extent; the new apparatus of Kessler, and the Gaillard tower have replaced platinum apparatus in modern works, and the platinum commands a high price as scrap.

Other forms of platinum apparatus have been described by F. Kalbfleisch,² M. Willett,³ C. Bartsch,⁴ G. Siebert,⁵ V. Hannelle,⁶ H. Howard,⁷ R. England,⁸ and others.

A point of importance in connection with the use of platinum stills is the corrosion of the metal by sulfuric acid. This has been mentioned by M. Davies,⁹ J. Conroy,¹⁰ M. Délépine,¹¹ L. Quennessen,¹² L. McCay,¹³ and W. Knocke.¹⁴ According to data collected by W. Heraeus, the loss of platinum per ton of strong acid is as follows:

1. Concentration to 92% H_2SO_4 : from 0.18 to 0.78 Gm.
2. Concentration to 93%–96% H_2SO_4 : from 0.3 to 1.3 Gm.
3. Concentration to 97%–98% H_2SO_4 : from 1.9 to 3.0 Gm.

The great differences shown probably depend partly on the varying quality of the platinum, a condition which shows no signs of improvement, and partly to the different nature of the firing and the impurities in the acid. Heraeus states that gold

1. A. Pohl, *Zts. ang. Chem.* 1912, **25**, 1852.
2. D. R. P. 1005, 1877; U. S. P. 267221; abst. J. S. C. I. 1883, **2**, 42.
3. E. P. 9362, 1884; abst. J. S. C. I. 1885, **4**, 499.
4. E. P. 6127, 1885; abst. J. S. C. I. 1885, **4**, 500. D. R. P. 35347; *Wag. Jahr.* 1886, **32**, 263.
5. E. P. 9514, 1893; abst. J. S. C. I. 1893, **12**, 690.
6. E. P. 22704, 1891; abst. J. S. C. I. 1893, **12**, 43.
7. E. P. 1762, 1897; abst. J. S. C. I. 1898, **17**, 47.
8. E. P. 22715, 1895; abst. J. S. C. I. 1896, **15**, 903. See also H. Glover, D. R. P. 10834; abst. *Wag. Jahr.* 1880, **26**, 234; J. A. C. S. 1880, **2**, 440.
9. J. S. C. I. 1894, **13**, 210.
10. J. S. C. I. 1903, **22**, 465; abst. *Chem. Centr.* 1903, **74**, II, 160; *Jahr. Chem.* 1903, **56**, 714.
11. *Compt. rend.* 1905, **141**, 886, 1013; abst. J. C. S. 1906, **90**, ii, 93; J. S. C. I. 1906, **25**, 314.
12. *Compt. rend.* 1906, **142**, 1341; abst. J. C. S. 1906, **90**, ii, 551; J. S. C. I. 1906, **25**, 695.
13. *Chem. Ztg.* 1912, **36**, 1072; abst. J. S. C. I. 1912, **31**, 928; C. A. 1912, **6**, 3242.
14. *Dingl. Poly.* 1859, **154**, 181; abst. *Jahr. Chem.* 1859, **72**, 714.

resists the action of acid better than platinum, a fact known to users of platinum stills, as these were always repaired with gold. The rate of attack is stated to be only one-seventh that of Pt. W. Heraeus prepared platinum stills covered with gold,¹ but since gold is now cheaper than platinum, this process has no apparent advantage.²

Concentration in Cascades. A modification of the series of glass retorts used by Gridley and Chance, already described, has been introduced by J. Hughes,³ consisting of a series of porcelain dishes with glass heads. An apparatus consisting of a series of porcelain capsules was constructed by C. Négrier & Co.,⁴ comprising two parallel rows of eight porcelain capsules, placed in terrace fashion, and delivering from dish to dish by means of spouts. Each pair of dishes on the same level was placed in depressions in a cast iron plate, with asbestos cloth interposed to minimize danger of breakage. The space below the dishes was heated by fire gases, the space above, which did not communicate with that below, carried off the acid fumes. The apparatus has been improved by H. Lemaitre.⁵

Another system is that of E. Hartmann and F. Benker.⁶ At first Benker used porcelain dishes covered with protecting cement, heated separately by several small fires, and enclosed in a chamber of volvic lava. In a later system the dishes were placed on supports of fireclay, being cemented in with asbestos and water glass, so as to completely separate the under and upper sides of the cascade. The heating is performed by a single large grate, burning coke or coal. There are 24 dishes in each of two cascades. In a more modern pattern, the porcelain dishes were replaced by cast iron. The preliminary concentration is carried

1. D. R. P. 63591; abst. Ber. 1892, **25**, 923. Zts. ang. Chem. 1903, **16**, 1201. See also E. Hartmann and F. Benker, Zts. ang. Chem. 1903, **16**, 1154. Chem. Fabrik Rhenania, D. R. P. 64572; abst. Wag. Jahr. 1892, **38**, 294; Zts. ang. Chem. 1892, **5**, 704; Mon. Sci. 1893, **42**, 163.

2. M. Neuerburg (D. R. P. 58511; abst. Wag. Jahr. 1891, **37**, 341) constructs pans of gold plated copper.

3. U. S. P. 339552; abst. J. A. C. S. 1886, **8**, 90.

4. E. P. 4171, 14022, 1890; abst. J. S. C. I. 1891, **10**, 46, 639. See A. Kretzschmar, Chem. Ztg. 1892, **16**, 418.

5. F. P. 357555; abst. Mon. Sci. 1906, **65**, 126.

6. Zts. ang. Chem. 1906, **19**, 564; 1909, **22**, 395; Chem. Ztg. 1899, **23**, 147; abst. J. S. C. I. 1899, **18**, 371; Chem. News, 1899, **80**, 295. J. S. C. I. 1902, **21**, 1344.

out in eight lead pans, arranged in two sets of four, and heated by waste gases from the cascades. These pans are made of special resistant lead ("Krellblei"), which withstands even boiling acid of 98%. The cascade dishes are of special cast iron, called "Neutraleisen," made by the A. G. für Bergbau und Eisenhüttenbetrieb at Kattowitz, Silesia, and are 320 mm. wide at the top and 165 mm. deep, placed on fireclay rings. Vitreosil dishes have also been used with success. The writer has been told, however, that the latter may develop fine cracks on use.

The Benker system consists of two parallel rows of neutral iron plates arranged in the form of a cascade, so that the acid flows down over them. These rest on the sides of a fire flue, conveying gases from a coke producer. The evaporating effect is said to be much greater than if quartz dishes are used. The vapors from the cascades are drawn off separately from each by a Kestner fan to a cooler. For the purposes of repair, each cascade may be used independently. Instead of the lead pans, the waste heat of the gases are now utilized in a lava tower, packed, and fed with chamber or Glover acid of 61°-62° Bé., and passes to the cascades. The fan draws the acid vapors from the tower through a cooler and coke filter. The final acid is 98% and water white. The system concentrates 10 tons of acid of 92%-93% H_2SO_4 per day, with a consumption of 12-14 cwt. of coke, or $5\frac{1}{2}$ -6 tons of 97%-98% acid with 22 cwt. of coke. The loss is 2% to 3% with 93% acid, and more with higher strengths. This is the main drawback to the cascade system; in some cases the writer has been informed that as much as 20% of the acid is lost, but this must be due to the neglect to scrub the fumes. Unless some fume scrubber is used, a cascade plant is a great nuisance on account of its fumes, a continual rain of small drops of acid being felt in its vicinity. With proper care, however, no bad effects can be noticed. In English works it has been usual in some cases to use vitreosil pans for the upper part of the cascade. At a certain point, ferric sulfate begins to separate out, causing bumping in vitreosil pans. Since the acid at this strength does not appreciably attack iron, cast iron pans are used beyond this stage. They are best covered, and the mud must be raked out of them from time to time.

Instead of using capsules or dishes, beakers were proposed

by T. Webb, of Manchester, England,¹ this system being adopted by J. Levinstein and others. Webb's apparatus consists of 14 or 16 glass or porcelain beakers arranged in cascades, each being 11 in. wide and 21 in. high, with large spouts, so that acid may flow from one beaker to the next below. From the last beaker the acid flows to a cooler, and thence to the storage tanks. A loose tapering glass tube is placed in each beaker, into which the acid flows. Much stress is laid on the assumption that the acid flowing into these tubes displaces stronger acid from the bottom of the beaker, which flows over the spout into the next tube. 14 beakers produce a carboy of acid of 1.838 sp. gr. from acid of 1.74, per hour, with the consumption of less than $\frac{1}{2}$ cwt. of coke. One man can attend to four sets of 14 beakers. To reduce breakages, the four bottom beakers were made of stoneware, and more recently all the beakers have been constructed of porcelain or stoneware, when breakage is slight. Double walled beakers have been specified.

J. Levinstein's apparatus differs from Webb's in the beakers having rounded bottoms, and being placed in metal dishes.²

Similar apparatus has been described by J. Bradbury,³ J. Scott,⁴ R. Wilson,⁵ M. Schwab,⁶ H. Green,⁷ J. Mackenzie,⁸ A. Nobel,⁹ O. Guttmann,¹⁰ K. Sundström,¹¹ R. Bithell and J. Beck,¹²

1. E. P. 1516, 1901; abst. J. S. C. I. 1902, **21**, 253. Belg. P. 160016, 1901. E. P. 2343, 17407, 18891, 1891. D. R. P. 135886; abst. Chem. Centr. 1902, **73**, II, 1437; Wag. Jahr. 1902, **48**, I, 307. Swiss P. 12551, 1896. U. S. P. 582329, 1897. D. R. P. 61752; abst. Wag. Jahr. 1892, **38**, 202.

2. E. P. 19213, 1892; 2476, 2835, 1893; 22844, 1894. D. R. P. 70407, 77331; abst. Wag. Jahr. 1894, **40**, 450, 451; Zts. ang. Chem. 1894, **7**, 533, 654; Ber. 1894, **27**, 918; 1895, **28**, 79.

3. E. P. 22327, 1893; abst. J. S. C. I. 1894, **13**, 251.

4. E. P. 14215, 1894; abst. J. S. C. I. 1895, **14**, 657.

5. E. P. 14221, 1895; abst. J. S. C. I. 1896, **15**, 544.

6. E. P. 22512, 1896; abst. J. S. C. I. 1897, **16**, 913.

7. E. P. 27209, 1911; abst. J. S. C. I. 1912, **31**, 488.

8. E. P. 6415, 1909; abst. C. A. 1909, **3**, 3001. See also E. P. 26278, 1904; abst. J. S. C. I. 1905, **24**, 196. E. P. 2389, 1912; abst. C. A. 1913, **7**, 2457.

9. D. R. P. 10145, 1880; abst. Wag. Jahr. 1880, **26**, 235.

10. E. P. 16220, 1898; abst. J. S. C. I. 1899, **18**, 275. D. R. P. 109247; abst. Zts. ang. Chem. 1900, **13**, 352; Chem. Ztg. 1900, **24**, 425; Wag. Jahr. 1900, **46**, I, 329; Mon. Sci. 1901, **57**, 17; 1907, **67**, 133. See Alkali Insp. Rep. **38**, 128.

11. U. S. P. 349414, 1886; abst. J. A. C. S. 1886, **8**, 237. See also A. Rappold and E. Leith, U. S. P. 260414, 1882.

12. E. P. 25526, 1913; abst. C. A. 1915, **9**, 1229; J. S. C. I. 1914, **33**,

the Fabrique de Scie Artificielle de T'ubize,¹ A. Bernutat,² P. Pfannenschmidt,³ J. Leitch,⁴ T. Kilroy,⁵ and J. Harris.⁶

Mackenzie's beakers are formed of basins with tubular pockets fitted internally with a loose circulating tube. The edge of the basin is curved inwards to prevent splashing.

F. Brown and the United Alkali Co.⁷ use basins with two spouts. The inlet spout of each basin rests on the edge of the seating of the basin next above, and the outlet spout rests in the inlet spout of the basin next below.

J. Carmichael and F. Guillaume⁸ use basins fitted with devices for discharging the acid mainly from the bottom of the basin. The device is separable from the basin, and consists of a half tube, preferably of semi-circular section, curved so as to lie with its edges against the sides of the basin, and extending from the bottom of the basin up to, over, and beyond the lip.

R. Lennox⁹ uses a heated inclined tube with notched weirs, down which acid flows. S. Tungay and G. Haughton¹⁰ employ square or oblong trays, with longitudinal or transverse channels or corrugations, to expose more heating surface. The trays may be made of any suitable material. J. Mackenzie¹¹ prefers Field

- 1207; Chem. Ztg. Rep. 1915, **39**, 219. E. P. 25892, 1913; abst. C. A. 1915, **9**, 1229; J. S. C. I. 1914, **33**, 1207; Chem. Ztg. Rep. 1915, **39**, 219.
1. E. P. 10386, 1915; abst. J. S. C. I. 1916, **35**, 537; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 180. Swed. P. 41077, 1916; abst. C. A. 1916, **10**, 3141. F. P. 479320, 1915; abst. J. S. C. I. 1916, **35**, 1016; C. A. 1916, **10**, 2281.
2. D. R. P. 281133; abst. J. S. C. I. 1915, **34**, 611; Zts. ang. Chem. 1915, **28**, 83; Chem. Zentr. 1915, **86**, I, 176; Chem. Ztg. Rep. 1915, **39**, 11; Ann. Rep. Soc. Ind. 1916, **1**, 111.
3. E. P. 13642, 1914; abst. C. A. 1915, **9**, 3337; J. S. C. I. 1915, **34**, 798. See also G. Siebert, D. R. P. 67863, 71586; abst. Wag. Jahr. 1893, **39**, 376; Zts. Chem. 1893, **6**, 299, 708; Ber. 1893, **26**, 558; 1894, **27**, 146.
4. E. P. 1495, 1915; abst. J. S. C. I. 1916, **35**, 308; C. A. 1916, **10**, 1916. E. P. 16001, 1915; abst. J. S. C. I. 1916, **35**, 689; Ann. Rep. Soc. Ind. 1916, **1**, 112. Swiss P. 74443; abst. Chem. App. 1919, **6**, 66; C. A. 1919, **13**, 2974. India P. 2423, 1916.
5. U. S. P. 1211594; abst. C. A. 1917, **11**, 1024; J. S. C. I. 1917, **36**, 214; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 180.
6. E. P. 7728, 1912; abst. J. S. C. I. 1913, **32**, 363; C. A. 1913, **7**, 2999; Chem. Ztg. Rep. 1912, **36**, 550. Cf. J. Morgan, E. P. 127652; abst. J. S. C. I. 1919, **33**, 575-A; C. A. 1919, **13**, 2421.
7. E. P. 110183, 1916; abst. J. S. C. I. 1917, **36**, 1227.
8. E. P. 15678, 1913; abst. J. S. C. I. 1914, **33**, 919.
9. E. P. 19573, 1912; abst. C. A. 1914, **8**, 557; J. S. C. I. 1913, **32**, 934.
10. E. P. 114072, 1917; abst. J. S. C. I. 1918, **37**, 260-A.
11. E. P. 2389, 1912. See Chem. Trade J. **51**, 459; abst. C. A. 1913, **7**, 869.

tubes, such as have been used in steam boilers, for constructing cascades. They are made of quartz or silicon-iron.

Vitreosil apparatus has been discussed by W. Mason,¹ A. Marshall,² and the English Alkali Inspector.³ The latter gives tables which will enable a cascade plant to be designed, of various materials, for any particular purpose. The data given by the firms interested is probably not so useful as this. For instance, the fuel consumption may be given for a concentration range well outside that needed, and it is well known that the fuel is highest for the last stages of the concentration.

CASCADE PLANT AND CONDENSERS
TABLE LXVII
BASINS OF SILICA, IRONAC, NARKI, AND TANTIRON, WITH PREHEATERS

| Acid Feed Strength °Tw | No. of Basins | Output Tons Acid per 24 Hours (166-169 °Tw) | Water and Acid Evaporated per 24 Hours Tons per 100 Basins | | | Packing in Condensers | | | |
|------------------------|---------------|---|--|-----|-----|-----------------------|---------------------|-----------------------------|---------------------|
| | | | Loss of Strong Acid Assumed to be | | | Per Basin | | Per Ton of Strong Acid Made | |
| | | | Nil. | 5% | 15% | Vol. Cubic Feet | Sec'l Area, Sq. Ft. | Vol. Cubic Feet | Sec'l Area, Sq. Ft. |
| | | | Coke Packing | | | | | | |
| 105° | 727 | 61.5 (= 1.69 cwt. per basin.) | 4.5 | 5.1 | 6.4 | 6.5 | 1.6 | 77 | 18 |
| 123° | 1440 | 112 (= 1.55 cwt. per basin.) | 3.1 | 3.6 | 4.7 | 8.2 | 0.7 | 105 | 10 |
| 136° | 40 | 4 (= 2.0 cwt. per basin.) | 2.7 | 3.3 | 4.6 | 6.2 | 1.2 | 62 | 12 |
| 147° | 100 | 15 (= 3.0 cwt. per basin.) | 2.9 | 3.8 | 5.5 | 7.5 | ... | 50 | ... |
| Ring Packing | | | | | | | | | |
| 120° | 40 | 2.5 (= 1.25 cwt. per basin.) | 2.5 | 2.9 | ... | 5.0 | ... | 76 | ... |

1. Met. Chem. Eng. 1915, **13**, 7; abst. J. S. C. I. 1915, **34**, 135; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111.
2. Met. Chem. Eng. 1915, **13**, 136; abst. C. A. 1915, **9**, 1372.
3. Alkali Insp. Rep. 1914; 1915; abst. Chem. Trade J. 1916, **59**, 303.

TABLE LXVII (Concluded)
 CASCADE PLANT AND CONDENSERS WITH PREHEATERS

| Acid feed, strength ° Tw. | Description of plant | Output of acid | | Packing in condensers | | | | | |
|---------------------------|--|-------------------|----------------|-----------------------|------------------|---------------------|-----------------------------|---------------------|--|
| | | Tons per 24 hours | Strength ° Tw. | Nature | Per basin | | Per ton of strong acid made | | |
| | | | | | Vol., cubic feet | Sec'l area, sq. ft. | Vol., cubic feet | Sec'l area, sq. ft. | |
| 110° | 3 tantiron pans and basins..... | 5 | 168° | coke | | | 43 | 7 | |
| 120° | 12 tantiron dishes (2 feet diameter)..... | 12 | 166° | bricks and tiles | | | 30 | .. | |
| 126° | 80 silica basins and 2 iron pots (8 feet x 3 feet) | 14 | 168° | rings | | | 15 | .. | |
| 135° | "Webb" plant, 30 vessels (3 cwt. per vessel) | 4.5 | 168° | coke and brick | 14.5 | 15.1 | 96 | 101 | |

The Gaillard Tower. The most successful apparatus yet introduced for the concentration of sulfuric acid on the large scale is without doubt the Gaillard tower.¹ This works on an entirely novel principle, which is both simple and ingenious. The apparatus consists of a vertical empty tower, of volvic lava or acid-resisting bricks, from the base of which a current of hot gas from a coke generator is directed upwards. Meeting this current of gas is a fine spray of acid to be concentrated, which is delivered

1. A. Gaillard, E. P. 23841, 1905; abst. J. S. C. I. 1906, **25**, 638; Chem. Ztg. Rep. 1907, **31**, 207. E. P. 12538, 1906; abst. C. A. 1907, **1**, 1640; J. S. C. I. 1907, **26**, 201. U. S. P. 856048; abst. Mon. Sci. 1908, **69**, 20. U. S. P. 859757; abst. Chem. Ztg. Rep. 1907, **31**, 433; Mon. Sci. 1908, **69**, 49. U. S. P. 859759. D. R. P. 192155; abst. Zts. ang. Chem. 1908, **21**, 796; Chem. Zentr. 1908, **79**, I, 315; Jahr. Chem. 1905-1908, I, 1616; Wag. Jahr. 1907, **53**, I, 339; Chem. Zts. 1908, **7**, 539. D. R. P. 205912, 1908; abst. C. A. 1909, **3**, 1805; Zts. ang. Chem. 1909, **22**, 648; Chem. Zentr. 1909, **80**, I, 804; Jahr. Chem. 1909, **62**, 488. F. P. 359442; abst. C. A. 1907, **1**, 630; Mon. Sci. 1906, **65**, 140; Chem. Zts. 1906, **5**, 135; J. S. C. I. 1906, **35**, 374. F. P. 367376, 1906; abst. Mon. Sci. 1908, **69**, 73; Chem. Zts. 1906, **5**, 545. F. P. 390807, 1908. Aust. P. 27339, 27691, 30457. Belg. P. 188081, 1905; 192889, 1906; 208289, 1908; 255536, 1913. Swiss P. 39050, 1907. In this connection see also Chem. Trade J. **42**, 60. G. Lüttgen, Chem. Ztg. 1910, **34**, 24. K. Recke, Chem. Ztg. 1910, **34**, 173, 182; abst. C. A. 1910, **4**, 1528. A. Hutin, Rev. Chim. Ind. 1918, **27**, 49; abst. C. A. 1918, **12**, 1816. Stolzenwald, Zts. ang. Chem. 1910, **23**, 1976. A. Düron, Zts. ang. Chem. 1910, **23**, 2307. A. Hutin and G. Pasque, Rev. Chim. Ind. 1918, **27**, 174; abst. C. A. 1919, **13**, 1622.

down the tower from sprays in the roof. Each fine drop of acid is exposed to the influence of the current of dry hot gas, and loses moisture rapidly. The drops of concentrated acid falling to the bottom of the tower are received in a strong lead saucer, like that of the Glover tower, where they coalesce, the liquid acid running away to a cooler. The hot moist gas from the top of the tower, which is taken away by a large lead main from the side, carries with it a dense mist of very fine droplets of acid, which must be recovered. It is first passed through an empty smaller lead tower, called a recuperator, down which part of the acid to be sent to the main tower is sprayed, and then passes to coke-box filters. A considerable improvement in the apparatus is the deposition of the acid mist by electrostatic precipitation--the so-called Cottrell method.

The earlier Gaillard tower arrangement corresponds roughly with the outline description given above. In this, the producer is charged with coke and is 3 m. high, 4 m. long, and 2.8 m. wide. The Gaillard tower itself, is 15.5 m. high, and consists of 15 rings of volvic stone, set one above the other without mortar. Each ring consists of 8 lava blocks, clamped by lead-covered iron rings. The blocks have V-shaped grooves, forming channels when two blocks are laid together. These channels are filled with putty formed of water glass and volvic powder. The tower at the bottom has an inner width of 1.70 m., at the top, but owing to the diminishing thickness of the walls, the width is 2 m. The thickness of the walls is 450 mm. at the bottom rings, 400 mm. at the fourth rings, 250 mm. at the three following rings, 200 mm. at the three following, and 150 mm. at the four top rings. The top of the tower is formed of four plates of lava, with an inlet for spray nozzles and a 500 mm. outlet for waste gases. The bottom of the tower is formed by a tray, 400 mm. high, with 12 outlets for the hot, strong, acid, and is cooled by a tubular cooler, 80 m. long, placed in the bottom tray round the tower.

The recuperating tower is of lead, 4 mm. thick, lined with 80 mm. stoneware plates. It is 8 or 10 m. high, 1.51 m. wide outside, and 1.34 m. wide inside. It is supported in a wooden or iron frame at such a height that its top is flush with the summit of the main tower. At the top are two spray nozzles and at the bottom an outlet for acid. The recuperator is connected

with the main tower by a volvic or stoneware pipe 0.5 m. wide, entering near the bottom.

After the recuperator, is the coke filter, a lead box covered outside with wood, 3 mm. thick, 3 m. high, 7 m. long, and 5 m. wide. The gases enter at the top and pass through graded coke resting on acid-proof bricks. The size of the coke varies from 60-100 mm. at the bottom to 5-15 mm. at the top. The gas is aspirated through the whole system by a fan.

The method of using the apparatus just described is as follows: The producer is charged every two or three hours with coke of 40 mm. size, which should be dry and free from non-coked coal, as the smoke will impart a brown color to the acid. The producer gas meets secondary air preheated by a firebrick grating, and the flame enters into the bottom of the tower. The acid spray is produced by a nozzle and air compressed to $1\frac{1}{2}$ atm. The concentrated acid flows through a cooler in the bottom tray, while the gases leave the top of the main tower and enter the recuperator at 100°-200°, and the acid mist is partially deposited to acid of 57° Bé. The gases then pass through the coke filter to the fan.

Gaillard guarantees the following results with his system, starting with chamber acid of 54° Bé.:

| Production in 24 Hours | Percentage H ₂ SO ₄ in Acid Produced | Consumption of Coke Per cent. of Acid Produced |
|---------------------------|--|--|
| 4 to 6 tons | 97-98 | 20-25 |
| 8 to 10 tons | 92-93 | 8-12 |
| 30 tons | 60° Bé. | 3-6 |

The great increase of fuel for production of strong acid, previously referred to in connection with the cascade system, is here quite apparent.

In case of acids forming crusts of ferric sulfate, Loewy and Klagsbrunn¹ collect the hot acid in an acid-proof dish at the base, from which it flows to an outside settler. This is a very obvious method of working, and is generally used, as will be described later. A. Düron² enriches the acid by SO₄ formed by dissociation by means of heated air, the waste heat of which is utilized in the

1. Aust. P. Ann. A-6792, 1909.

2. F. P. 430145; abst. Mon. Sci. 1913, **79**, 127.

recuperator. The Swedish Nitro Syndicate¹ and H. Klink² use a packed tower.

The high pressure hard lead fans of Kestner are now largely employed in connection with Gaillard installations.³ Instead of a coke producer, O. Zahn's⁴ high-pressure gas producers may be used.

The Gaillard tower was adopted in the large British acid plants at Queen's Ferry and Gretna,⁵ but in a considerably improved form. It was larger, built of acid-resisting bricks, specially shaped and set with silicate mortar, and the gas outlet was not through the dome, but from the side at the top. The acid was collected in a large lead dish at the base of the tower, from which it ran to mud settlers, and cooling spirals. Gaillard's method of cooling in the base of the tower was abandoned. A brief description of the new towers is given by J. Partington.⁶ It is there stated that a tower 60 ft. high and 5 ft. diameter produces 40 tons of 95%–96% acid per 24 hours, with a loss of 3%–5%. The consumption of coke is 1½–2 cwt. per ton of strong acid. The tubular scrubber described is no longer used. Details of the Gretna installation are given in the next topic.

In later towers, the loss has been reduced to less than 1%. Much trouble was experienced by corrosion of the lead mains leading the hot gases from the top of the tower. These might be replaced by stoneware mains, as in the original Gaillard tower.⁷ The single spray jet at the top of the tower was replaced by three powerful Koertzing jets of hard lead, and a large Kestner fan was used to draw the gases through the apparatus. The fan at Queen's Ferry was the largest of its kind ever erected. It was

1. E. P. 10591, 1909; abst. J. S. C. I. 1910, **29**, 88. E. P. 402078; abst. J. S. C. I. 1909, **28**, 1197.

2. U. S. P. 1276377; abst. C. A. 1918, **12**, 2133; J. S. C. I. 1918, **37**, 654-A.

3. R. Forster, Chem. Ztg. 1910, **34**, 734; abst. Chem. Zentr. 1910, **81**, II, 504.

4. D. R. P. 190660, 237238; abst. Wag. Jahr. 1908, **54**, I, 144.

5. See Exptl. Rep. 76, 77, 113, H. M. Factory Gretna (Dornock).

6. "The Alkali Industry," 1918, 33.

7. For further information regarding the Gaillard system consult A. Hofmann, Zts. ang. Chem. 1910, **23**, 3122. Similar systems are described by H. Harris, E. P. 7728, 1912. J. Harris and D. Thomas, E. P. 23414, 1914. E. Armstrong, J. Ind. Eng. Chem. 1917, **9**, 386; abst. J. S. C. I. 1917, **36**, 501. E. Froid, U. S. P. 859757; abst. C. A. 1907, **1**, 2760. H. Bach, Chem. Ztg. 1910, **34**, 267; abst. C. A. 1910, **4**, 1398.

found that concentration of the acid occurred as soon as the drops entered the tower, as the condensate in the outlet main was practically the same strength as that in the saucer. If the temperature of the gases entering the recuperators was kept low (180° – 190°), so that no acid need be run down, it was found that 80% acid condensed. In making 92%, about 5% of the total acid charged to the tower appeared in the recuperator.

The scrubbing of the mists from the Gaillard towers is a problem not confined to that type of apparatus, so that it is left to a later section. It may be said that the most efficient system yet used is that of electrostatic precipitation.

Gaillard Towers at Gretna Plant. From the exhaustive report of V. Gloag and J. Riley, the following facts in respect to the Gaillard installation at H. M. Explosives Factory, Gretna, Scotland, are taken.

The plant comprizes two houses of eight independent units, each consisting of (a) Main tower; (b) Recuperator; (c) Scrubber; and (d) Fan. The units in each house deliver into a separate fume main leading to the Cottrell precipitator (see p. 1393).

Main Tower is 47' high from the base to the springing of the dome, and is built of concentric rings of joggle-jointed, acid-proof blocks, 3" thick, bound together by mild steel hoops 2" apart. The lower 13' 6" of the tower is 8' 6" internal diameter and consists of six rings; the internal diameter of the rest of the tower being 9' 6". The next 10' 5" consists of 5 rings only, after which follows 11' 8" with only 4 rings, and the remainder of the towers with 3 rings. The reduction in number of rings is made by completing the outer ring with a bonder course.

The floor of the tower is sloping, and discharges into a cylindrical mud-box, 4' 6" diam. and 4' 6" deep, built of acid-proof blocks. An opening 15" x 2' 2" at the base of the tower, just above the mud-box, and normally closed by a loose slab, enables sludge to be raked from the floor of the tower. Both tower and sludge-box stand in a dish of 30-lb. lead. The original run-offs from the sludge-boxes were at first constructed of cast iron, but on account of their rapid disintegration, have been replaced by Narki run-offs.

Tower Dome. This springs from a springer block course, and is struck to a radius of 7' 5", having a 24" outlet, and pockets

for the atomizers or sprays, the number being originally five, which was subsequently increased to nine. The life of a dome is intimately connected with its treatment. A positive gas pressure on the dome means leakage of gas, sweating of acid and failure of dome. This has been obviated by elimination of throttling in the down take from the tower, which results in a suction at the top of the tower.

Tower Off-takes. After leaving the main tower, the gases are led to the base of the recuperator by means of a 2' diameter acid-proof, stoneware pipe, covered with 8-lb. lead, the pipe standing in a brick base. The 24" off-takes are taken centrally from the dome and led into the top of the recuperators, a special brick dome being fitted to receive it. A concurrent flow of acid and gas thus exists in the recuperator.

The off-take has been erected both in Narki and lead-covered pottery, the Narki pipes being about thrice as expensive, but possess the advantage over pottery in that cracks do not appear resulting in leakage of hot acid. The main advantage of these take-offs is:

(a) Complete absence of throttle to flow of gases.

(b) When the slope of the off-take is increased to $3\frac{1}{2}''$ to the foot, this assures that any acid condensing in the off-take will readily drain into the recuperator, instead of remaining in the off-take, and ultimately finding its way through the cracks to the lead work.

Recuperator. This consists of a lead-covered tower 30' 8", high and 5' external diameter, built of acid-proof blocks, the lower 14' 4" consisting of two rings, and the remainder of one ring, the lower part having an internal diameter of 4', and the upper of 4' 6". The whole is built of a base-plate of acid-proof blocks standing in a lead saucer, the bottom course being constructed so as to allow the acid to overflow into a launder at a level of $2\frac{1}{2}''$ from the base of the tower. The top of the recuperator has four atomizer holes.

The main sources of trouble in connection with the recuperators are:

(a) Leakages at the base in the pottery junction pipe from the main tower down-take, which may temporarily be overcome

by burning a lead fender between the recuperator and the base block of the down-take.

(b) Leakages in the first 10' from the base, due to the existence of an inner lining of tiles up to this level. The acid working behind this, ultimately makes its way through to the lead work, making necessary the repointing of these points.

The gases are led from the recuperator through a 15" outlet into a lead conduit, expanding to 24", to the bottom of the scrubber, this recuperator off-take giving considerable trouble. Pottery bends have been found much more satisfactory than those constructed of lead.

Scrubber. Consists of a 30' x 16' x 11' box, lined with 10-lb. lead, and supported by the necessary wood-work. Gas enters the end of the scrubber at the bottom through an opening 4' 9" x 15", and leaves through an 18" diameter outlet in the top cover. In some instances the gas is introduced into the scrubber through a 24" pipe, which passes through the top and discharges at the bottom of the scrubber. Experience shows that there is a tendency for the down-take to develop holes immediately under the scrubber top, thus short-circuiting the gas, with resulting poor scrubbing and the development of high temperatures.

The bottom of the scrubber is covered with acid-proof tile on which brick grid-work is built, to carry the coke and obtain even distribution of gas. As the coke is filled in, the scrubber is lined with 1½" tile to a height of about 6'. After carefully filling the spaces left by the checker-work with large coke, the main filling is packed with 8" to 1½" coke, the remainder, with screened coke varying uniformly from 1½" at the bottom to ¾" at the top. If available, coke as fine as ⅛" is recommended.

To reduce the temperature at the fan, and thus obtain increased output, the flooding of scrubber tops has been resorted to, a cooling of 15°-20° being thus obtained.

Fans. The gases are drawn through an 18" main from the top of the scrubber to the Kestner, high pressure, belt-driven fans, which deliver them through an 18" diam. conduit into the Cottrell flues. The fans in operation are the 16" and 21" types. Fans of the former size have an average life, after careful balancing, of 6 months at 1500 r. p. m., while the average life of the 21" fans have been 2 months at 1000 r. p. m. The usual

cause of break-down has been the "springing" of the blades, the reason being the composite nature of the impeller, the blades being bolted on to the boss.

Furnace. The producer gas is drawn from the 3' x 4' main flue through a water seal valve, to the furnace flue 2' x 3', and passes through an 8" mushroom valve to the furnace. Here it meets with the primary air, and is burned in a combustion chamber 5' 6" x 6' x 4', through two gas ports 9" x 4' $\frac{1}{2}$ ", and is drawn up a canister 4' x 3' 6" x 9' high, filled to a height of 4' 9" with checker brick work. Just before entering the canister, the gases admix with the secondary air, which enters between the secondary arch and the main furnace arch. The entire structure is sheathed in steel and lined with firebrick. Air is admitted separately from the gas, and the third central gas valve is adjusted so as to maintain a dull red heat on the checker work through which all air is admitted. No unburned CO has been determined in the burned gases.

Acid Circulation. Weak acid from the denitrated acid tanks gravitates through a 6" lead line to two houses, each being supplied by a 4" line, and this again divides into two 3" lines, which feed the blow casks, 8 for each house. These are 18' 6" long and 4' 2" inside diam., built in 3 sections and lined with 12-lb. lead.

The acid is blown from the eggs by air at a pressure of 80 lbs. per sq. in., through 1 $\frac{1}{2}$ " rising mains, to the atomizers at the top of the towers. Two eggs supply each pair of towers, one egg filling, and one egg blowing, the recuperators being fed from these eggs at the same time. The acid passed down the main tower in the form of mist is concentrated by the hot furnace gas, and finally delivered through the sludge-box to the cooler. The original design consisted of a cylinder 3' 2" internal diam. and 3' 11" deep, made of cast iron 1" $\frac{1}{2}$ " thick, to which is fitted a steel water-jacket, 3' 11 $\frac{3}{4}$ " diam. and 3' 1" deep. Three concentric 1" lead cooling coils are fitted in the cooler 14", 23" and 32" in diameter, giving a cooling surface without the jacket of 113.5 sq. ft.

The acid leaving the coolers is stored in one of the 12 storage tanks, of which six are attached to each house. These are 20' x 12' x 3' deep, consisting of 12-lb. lead supported by a wooden framework. Each tank has a 2" outlet, from which the acid

passes to two 10" Regs Roturbo pumps in each house, which deliver the acid along steel mains to the storage tanks of the acid mixing plant. The acid from the recuperators is collected in a cooling launder, and led through coolers to the recuperator acid tanks.

Concentration by Electricity. In places where electric power is cheaply generated, say by water power, there should be some possibility of effecting the concentration of sulfuric acid by running it in thin layers over grids heated by a current. If the grids are not insulated an alternating current would be used to prevent electrolysis. A. Bucherer¹ computes that, for the production of 1 metric ton of acid of 66° Bé. from 1170 kgm. of acid of 60° Bé., 442 electrical H. P. H. will be required. C. Häussermann and F. Niethammer² find by experiment that very much more energy than the above is actually used. S. Peuchen and P. Clarke³ advocate revolving or stationary electrodes for the purpose. L. Wacker⁴ and S. Pagliani⁵ also propose electrical methods.

Concentration in Vacuum Pans. A method of concentrating sulfuric acid in vacuum pans has been described by A. de Hempinne,⁶ but, it is understood, was not successful. In the apparatus of G. Krell,⁷ the acid enters a lead pipe stiffened inside by diaphragms, heated in an oil bath. The acid passes through in a zig-zag course, and hot gases may be introduced by a perforated pipe. Some of the diaphragms are perforated only under the acid, and divide the vapor space into three compartments, con-

1. Chem. Ztg. 1893, **17**, 1597; abst. J. S. C. I. 1894, **13**, 249; Jahr. Chem. 1893, **46**, 313.

2. Chem. Ztg. 1893, **17**, 1907; abst. J. S. C. I. 1894, **13**, 391; Jahr. Chem. 1894, **47**, 408.

3. E. P. 24739, 1893; abst. J. S. C. I. 1894, **13**, 251.

4. E. P. 3183, 1895; abst. J. S. C. I. 1895, **14**, 484; Jahr. Chem. 1897, **50**, 514; Chem. Ztg. 1896, **20**, 591; Mon. Sci. 1897, **50**, 30.

5. Ann. Chim. Appl. 1918, **10**, 134; abst. C. A. 1919, **13**, 994; J. S. C. I. 1919, **33**, 171-A.

6. See Bull. Musée Ind. Belg. Jan. 1882.

7. D. R. P. 118880; abst. Zts. ang. Chem. 1901, **14**, 423; Chem. Centr. 1901, **72**, I, 865; Jahr. Chem. 1901, **54**, 242; Chem. Ztg. 1901, **25**, 381; Wag. Jahr. 1901, **47**, I, 412. D. R. P. 166557, 176994; abst. Zts. ang. Chem. 1906, **19**, 1943; Chem. Centr. 1906, **77**, I, 418; Jahr. Chem. 1905-1908, I, 1615; Wag. Jahr. 1905, **51**, I, 396; Mon. Sci. 1907, **67**, 58; Zts. Schiess. Spreng. 1906, **1**, 49. F. P. 363604. Aust. P. 21305. Belg. P. 145168, 1899; 177734, 1904. See also D. R. P. 83540; abst. Wag. Jahr. 1895, **41**, 394; Chem. Ztg. 1895, **19**, 2084.

nected through to a common vacuum pipe. Coolers are provided to condense acids of different strengths. A preheater of obvious construction is provided. So far as aware, this apparatus has never been used.

The cast iron vacuum retorts successfully used in Germany for concentrating sulfuric acid weigh about $7\frac{1}{2}$ tons. The reduced temperature in these retorts renders them suitable for treating the impure acid formed in petroleum refining, when there is less loss as SO_2 than in open pans. The organic matter is coagulated and can be filtered off through sand. A. Cocking and G. Kynoch & Co.¹ also use cast iron vacuum retorts for concentrating waste acid from nitroglycerol. The Kommanditgesellschaft L. Kaufmann & Co.² concentrate sulfuric acid in a cast iron vacuum still by means of a steam jacket or gaseous fuel. The acid is propelled in thin layers, 10-15 mm. deep, by means of stirrers over the heating surface. The Norsk. Hydro-Elektrisk Kvaelfstof. A. G.³ employ a series of vacuum stills on the tubular principle, in the first of which the acid is brought up to 60%-69%, in the second to 75%, and in the third to 79% SO_3 . F. Girod and the Gräflich von Landsberg-Velen und Gemensche Chemische Fabrik, Berg-und Hüttenwerke,⁴ concentrate in lead pans to about 61° Bé. at a temperature of 150°-160°, and then atomize the acid in a tower at a reduced pressure, preferably about 20 cm. Hg. The acid is collected in lead pans arranged in cascade and heated by hot air. J. Patten⁵ feeds the acid successively through a series of lead-lined chambers heated interiorly by steam coils and in which a vacuum is maintained to distil off the water at a low temperature. The patent relates especially

1. E. P. 28891, 1896; abst. J. S. C. I. 1897, **16**, 1040.
2. D. R. P. 134773; abst. Zts. ang. Chem. 1902, **15**, 1098; Chem. Centr. 1902, **73**, II, 1022; Chem. Ztg. 1902, **26**, 986; Wag. Jahr. 1902, **48**, I, 309; Mon. Sci. 1903, **59**, 73. Concentration in lead pans under vacuum is described by J. Meyer, D. R. P. 71580; abst. Wag. Jahr. 1893, **39**, 375; Zts. ang. Chem. 1893, **6**, 707; Wag. Jahr. 1893, **39**, 375.
3. D. R. P. Anm. N-15431. F. P. 474995, 1914; abst. Chem. Ztg. 1916, **40**, 146; Mon. Sci. 1916, **83**, 83. E. P. Appl. 1637, 1919; abst. J. S. C. I. 1919, **38**, 94-A.
4. F. P. 432873, 1911; abst. J. S. C. I. 1912, **31**, 127; Mon. Sci. 1913, **79**, 130. Belg. P. 237785, 1911. Aust. P. Anm. 6788/11; abst. Chem. Ztg. 1913, **37**, 76. See also F. Girod, E. P. 17158, 1911; F. P. 432873, 1911; abst. J. S. C. I. 1912, **31**, 127, 335; C. A. 1913, **7**, 403; Chem. Ztg. Rep. 1912, **36**, 380; Mon. Sci. 1913, **79**, 130.
5. U. S. P. 1286080, 1286188; abst. C. A. 1919, **13**, 250; J. S. C. I. 1919, **38**, 718-A.

to constructional details for supporting the upper part of the lead lining to prevent its premature destruction.

The Manufacture of Monohydrate. Monohydrate, or 100% H_2SO_4 , has already been described. W. Mayers¹ proposed to pass burner gas through sulfuric acid so as to dissolve the SO_3 in the latter, and bring up its strength. G. Lunge² proposed to separate crystals of monohydrate from C. O. V. by freezing the latter. The process was worked for many years³ in England, France and Germany, but was abandoned with the introduction of the contact process. By this latter method SO_3 is made, which may be added to C. O. V. to bring it to exactly 100% strength. Freezing methods have also been described by H. Osterberger and E. Capelle,⁴ M. Morance,⁵ and A. Donk.⁶

The modern process is ascribed to H. Weber⁷ and consists in passing SO_3 into sulfuric acid. A Düron⁸ decomposes H_2SO_4 by heat into SO_3 and H_2O . The former is absorbed in conc. H_2SO_4 . C. Daub and J. Deuther⁹ describe a reaction apparatus for the contact process.

Concentration in a Current of Gas. J. Stoddard¹⁰ and J. Galletly¹¹ proposed to assist the evaporation of water from acid heated in lead pans by forcing a current of cold air through the acid. The use of hot air was first applied by Gossage in 1850, who used a double shelled lead tower with an air space between the shells. The tower was packed with pebbles, over which the acid trickled,

1. E. P. 1201, 1878; abst. J. A. C. S. 1879, **1**, 296; Wag. Jahr. 1879, **25**, 287.

2. E. P. 96, 1883; abst. J. S. C. I. 1883, **2**, 414; Wag. Jahr. 1884, **30**, 200. See also J. Brock, E. P. 4430, 1887; abst. J. S. C. I. 1888, **7**, 209; Chem. Centr. 1888, **59**, 880.

3. See Cosmos, 1909, **60**, 414.

4. Bull. soc. ind. Rouen, 1889, **17**, 307; abst. J. S. C. I. 1890, **9**, 390, 507.

5. Compt. rend. 1909, **148**, 842; abst. C. A. 1909, **3**, 1913; J. S. C. I. 1909, **28**, 520.

6. Chem. Weekblad, 1913, **10**, 956; abst. C. A. 1914, **8**, 1926; Chem. Zentr. 1914, **85**, I, 105.

7. U. S. P. 1233626; abst. C. A. 1917, **11**, 2601.

8. E. P. 430145; abst. Mon. Sci. 1913, **79**, 127.

9. E. P. 9536, 1902; abst. J. S. C. I. 1902, **21**, 1138.

10. Chem. News, 1871, **23**, 167; abst. Poly. Centr. 1871, **37**, 914; Chem. Centr. 1871, **42**, 354; Chem. Tech. Rep. 1871, **10**, I, 130; Dingl. Poly. 1871, **200**, 419; Jahr. Chem. 1871, **24**, 1010; Wag. Jahr. 1871, **17**, 220. See also F. Bode, Dingl. Poly. 1871, **201**, 45.

11. Chem. News, 1871, **24**, 106; abst. Chem. Centr. 1871, **42**, 602; Chem. Tech. Rep. 1871, **10**, II, 126; Dingl. Poly. 1871, **201**, 538; Jahr. Chem. 1871, **24**, 1010; Wag. Jahr. 1871, **17**, 227.

while a current of air, very strongly heated in iron pipes, passed upwards through the tower. A similar apparatus has been described by M. Cotelle.¹ Other types of concentrators, based on this principle, were described by S. McDougall,² the International Vacuum-Eismachinen-Verein,³ R. Finch,⁴ E. Fontenille,⁵ J. Gridley,⁶ F. Falding,⁷ W. Quinan⁸ and G. Davis.⁹

The first really successful apparatus based on this principle, which has been largely used, is that of J. Kessler,¹⁰ and has been installed in a number of works, being probably the best type unless large amounts of acid have to be dealt with, when the Gaillard tower is undoubtedly to be preferred.

The conditions to be satisfied in the apparatus are as follows: The current of heated gas must be brought into intimate contact with a surface of liquid sufficiently large to cause a rapid reduction of temperature of the gas. The air or gas then becomes completely saturated with moisture and acid vapor. The apparatus must resist the action of the hot gas and acid, and the crusts which inevitably form must be capable of being removed without difficulty. Under these circumstances the acid may be concentrated far below its boiling point. In order to produce acid of 95% strength, boiling at 284°, a temperature of 170°-180° is sufficient, while for the most concentrated acid, boiling at 320°, the temperature need not exceed 200°-230°.

The Kessler apparatus in general, comprizes the following:

1. Mon. Sci. 1869, **11**, 63; abst. Chem. News, 1869, **20**, 107; J. Pharm. 1869, (4), **10**, 32; Jahr. Chem. 1869, **22**, 1030; Wag. Jahr. 1869, **15**, 169.
2. U. S. P. 289293; abst. Wag. Jahr. 1884, **30**, 299.
3. D. R. P. 33172; abst. Wag. Jahr. 1885, **31**, 951.
4. E. P. 2207, 1886; abst. J. S. C. I. 1887, **6**, 216; J. Soc. Dyers Col. 1886, **2**, 49. See also C. Barbiaux, Belg. P. 233585, 1911.
5. D. R. P. 37713; abst. Wag. Jahr. 1887, **33**, 508.
6. U. S. P. 240248; abst. J. A. C. S. 1881, **3**, 69.
7. E. P. 17602, 1893; U. S. P. 541041; abst. J. S. C. I. 1893, **12**, 1032; Mon. Sci. 1894, **44**, 918.
8. U. S. P. 699011; abst. J. S. C. I. 1902, **21**, 772; Mon. Sci. 1902, **58**, 179; Chem. Zts. 1903, **2**, 8.
9. E. P. 128396; abst. C. A. 1919, **13**, 2977; J. S. C. I. 1919, **38**, 484-A.
10. E. P. 19215, 1891; abst. J. S. C. I. 1892, **11**, 434. E. P. 26769, 1898; abst. J. S. C. I. 1900, **19**, 246. E. P. 21376, 1900. Cf. Alkali Insp. Rep. **33**, 74, 146. Aust. P. 8055, 1902. See also Alkali Insp. Rep. 1903, **40**, 24; 1904, **41**; 1905, **42**, 20; 1910, **47**, 17; 1914, 1915. Mon. Sci. 1904, **61**, 557. D. R. P. 69216; abst. Wag. Jahr. 1893, **39**, 376. F. R. 283752 and addition, 3384, 1904; 305781 and addition 3385, 1904; U. S. P. 520994, 1894. Belg. P. 136581, 1898; 150225, 1900. J. Kessler and C. Ferrand, Swiss P. 4693, 1892. J. Kessler, U. S. P. 651717, 1900; U. S. P. 680867, 1901. Faure & Kessler, D. R. P. 6972; abst. J. A. C. S. 1879, **1**, 501.

The lower part is called the saturex; and here the gases enter at 300°-450°, and leave at 150°. It consists essentially of a shallow trough of volvic lava or acid-resisting stone, enclosed in a thick lead jacket. Between the bottom and cover of the saturex are several thin partitions, which cause the fire gases to pass closely over the surface of the acid, and when passing from one of these flues to the other, through the acid itself. The gases are quickly reduced to a temperature of 150°, while the acid loses water, and some acid vapor, and runs out in a concentrated state to the cooler. The hot gas is introduced through a cast iron pipe, which is flattened below so as to occupy the whole breadth of the saturex.

The steam and acid vapors from the saturex pass to the upper part of the apparatus, called the recuperator, consisting of three lower stone plates and two upper lead plates, arranged so as to form a bubbling column like a rectifying still. Each plate has 100 holes with slightly raised margins, so that a layer of acid always remains on it. Each hole is covered with a porcelain bell with serrated edges, producing a resistance to the passage of gas. The acid to be concentrated arrives through a pipe and runs by overflows from plate to plate, until it finally arrives at the saturex.

The gases from the saturex are drawn by a fan, or souffleur, through the recuperator, bubbling through the inverted cups, and thus coming into intimate contact with the weak acid. The thermometers ought to read 150° and 85°, respectively. The pressure is registered by a gauge, and the gases pass out by a pipe to the filters. The concentration may be taken to 98%, and impure Glover acid may be used, as there is no crust formation in the recuperator. The crusts in the saturex may be removed from time to time through the cleaning holes. The hot gases are made in a small producer burning coke. The fuel consumed is 8 parts of small gas-coke for the producer, and 3-4 parts of coal for raising steam for the fan, per 100 parts of acid of sp. gr. 1.838 from acid of 1.58. No weak acid is produced.

A modified apparatus of Kessler was patented in 1900. It is called a "Radiateur, and consists essentially of fireproof slabs heated above, and radiating heat upon the surface of acid below. In these is a fireplace for coke or coal, and flues through which

the fire gases pass on their way to the chimney. The heat is radiated from an arch on to slabs. The gases rise into a flue, which is covered with cast iron plates, upon which stand the lead pans for carrying out the preliminary concentration.

The initial acid is contained in a flat trough of lava or other refractory material, with joints of asbestos cement. This is surrounded by a lead jacket which rests on iron rails. The surface of the acid is kept from 2 to 6 cm. from the slabs by means of a valve in the inlet pipe. The acid flows from the pans through a siphon and pipes into an acid-proof box packed with pieces of quartz, and covered outside with sheet lead. The vapors pass through this box; those which are not condensed pass to a second box made of lead and packed with graded coke, the small pieces being as large as grains of wheat. This coke is put in dry. The weak acid caught in these scrubbers passes through into pans. The draft is produced by an injector in a vertical pipe so as to balance the suction of the chimney. The acid passes through a lead cooler into a lead pot. The run-off pipe is of lava covered with lead, burnt on one side to the acid dish and on the other to the cooler.

The filters for removing acid mist are very important.¹

The draft through the Kessler apparatus is best derived from Kestner hard-lead fans, which are much superior to steam injectors or cast iron Pratt fans.² They are best placed at the end of the apparatus, after the coke box filters, or between these and the saturex.

A new type of Kessler apparatus is that of J. Teisset and L. Prat.³ In this the longitudinal baffles of the old apparatus are replaced by transverse baffles, a fan draws the gases through the apparatus, and a regenerator is used. The fire gases from the regenerator pass through the saturex, which is a pan of volvic lava in a lead shell. The transverse baffles rest on bearers, and dip a little into the acid. A fan and ejector⁴ placed externally

1. See Chem. Trade J. 1907, **40**, 80. P. Meyer, Zts. ang. Chem. 1906, **19**, 1318.

2. R. Forster, Chem. Ztg. 1910, **34**, 734; abst. C. A. 1910, **4**, 2182.

3. U. S. P. 993125; abst. J. S. C. I. 1911, **30**, 748; Mon. Sci. 1911, **77**, 18. F. P. 398212, 1908; abst. J. S. C. I. 1909, **28**, 937. E. P. 14300, 1909; abst. J. S. C. I. 1910, **29**, 950. D. R. P. 229676; abst. C. A. 1911, **5**, 2535; Zts. ang. Chem. 1911, **24**, 184; Chem. Zentr. 1911, **82**, I, 274; Wag. Jahr. 1911, **57**, I, 421; Chem. Ztg. Rep. 1911, **35**, 54.

4. E. P. 13720, 1909.

draws out the gases, which pass under the baffles, and thoroughly agitates the acid. The recuperator is of an improved type, with six horizontal plates with numerous holes covered with bells. The acid runs in at the top, and the gas temperature is reduced to 90° at the top of the recuperator. At this temperature only aqueous, but no acid, vapor can exist, so that only a little acid fog escapes. This is retained by a coke filter, while the saturator is cleaned through stoppered holes. The concentrated acid, of 98% H_2SO_4 , runs from the saturator to the cooler. The consumption of coke is 18%-20%.

J. Gazel¹ gives the following particulars of a Kessler apparatus supplied to a British explosive works in 1898:

| | |
|------------------------------------|-----------|
| Strength of feed acid..... | 48° Bé. |
| Strength of concentrated acid..... | 65.9° Bé. |
| Production per day..... | 9100 kgm. |
| Coke for gas producer..... | 650 kgm. |
| Coal for steam raising..... | 750 kgm. |

The improvement in the new apparatus is ascribed by G. Lüttgen² to acid waves formed by the hot gases passing through, and impinging on the walls so that splashing and spraying are produced. F. Stolzenwald³ doubts this.

P. Vialleix and F. Perrin⁴ also describe a modification of the Kessler apparatus, in which the saturator consists of a single central channel and two side channels through which the hot gases are aspirated. The recuperator contains a number of superposed trays with projections touching the surface of the acid in the lower trays, and passages for the gas. The acid overflows from tray to tray in a zig-zag path. The trough and trays are constructed of lava or stoneware. Vitreosil has been proposed⁵ instead of lava for the apparatus, but would doubtless be far too fragile for the purpose.

A. Zanner⁶ uses cast iron pans lined with acid-proof slabs,

1. Mon. Sci. 1907, **66**, 368.
2. Chem. Ztg. 1910, **34**, 24; abst. Jahr. Chem. 1910, **63**, I, 527; Wag. Jchr. 1910, **56**, I, 423.
3. Zts. ang. Chem. 1910, **23**, 1976; abst. Chem. Zentr. 1910, **81**, II, 1957.
4. E. P. 8142, 1911; abst. J. S. C. I. 1912, **31**, 187; C. A. 1912, **6**, 2825. F. P. 420543; abst. J. S. C. I. 1911, **30**, 360. U. S. P. 1066557, 1913; abst. J. S. C. I. 1913, **32**, 791. Belg. P. 232980, 1911. Cf. F. P. 397080, 1908.
5. A. Pohl, Zts. ang. Chem. 1912, **25**, 1851.
6. E. P. 2370, 1902; U. S. P. 693635, 1902; 768108, 1904; abst. J. S. C. I. 1902, **21**, 470. See Zts. ang. Chem. 1907, **20**, 8. E. Hagmann and

placed in the flues from the burners and receiving Glover tower acid. The apparatus consists of a flue containing the pans on cast iron girders, the pans being lined with stoneware plates cemented with water glass and asbestos. The corners are secured by stones, so that no primary joints are exposed to the acid. To prevent contamination with dust, the pans are covered with perforated iron or fireclay slabs provided with caps. The acid is fed through a porcelain lined iron tube, leaving the apparatus by a cast-on lip lined with stoneware. The steam and acid vapors pass on into the Glover tower.

The Norsk. Hydro-Elektrisk Kvaestofaktieselskabet¹ run the acid through a tower heated by steam, and remove the water from the acid in three stages by using steam under 3, 4 and 5 atm. pressure. They also describe concentration by distillation, cooling the vapors and treating them with a drying agent. P. Pritchard and the United Alkali Co.² have devised a tubular apparatus heated by steam.

H. Freidrich³ describes a concentration apparatus consisting of a still holding a large quantity of boiling 66° Bé. acid, on the surface of which a small amount of Glover acid is allowed to trickle, while the concentrated 66° Bé. acid is run off from the bottom of the still. This, of course, is the well known method of Gridley, and is devoid of novelty. The same inventor suggests erecting a small tower similar in construction to the Glover after the concentration system, allowing the hot acid vapor to pass up the tower against a stream of chamber acid, so that the vapors leave at 100°. This again is a well known process, although it was controverted by G. Bruhn.⁴

C. Grosse-Leege⁵ passes a current of hot gas tangentially to the walls above the surface of the acid, so as to produce a spiral

F. Benker, Zts. ang. Chem. 1906, **19**, 566. See also F. Meyer, J. S. C. I. 1903, **22**, 781.

1. F. P. 459092; abst. C. A. 1914, **8**, 2463; Chem. Ztg. Rep. 1914, **38**, 170; Mon. Sci. 1914, **81**, 73. Swiss P. 64234. E. P. 132704; abst. J. S. C. I. 1919, **38**, 817-A.

2. E. P. 29542, 1913; abst. J. S. C. I. 1914, **33**, 1207.

3. Chem. Ztg. 1909, **33**, 478, 634; abst. Chem. Eng. **10**, 14; C. A. 1909, **3**, 2036, 2352.

4. Chem. Ztg. 1909, **33**, 812; abst. C. A. 1911, **5**, 2863.

5. D. R. P. 176370; abst. Chem. Centr. 1906, **77**, II, 1668; C. A. 1907, **1**, 1171; Zts. ang. Chem. 1907, **20**, 893; Jahr. Chem. 1905-1908, I, 1616; Chem. Ztg. Rep. 1906, **30**, 371; Wag. Jahr. 1906, **52**, I, 391; Mon. Sci. 1908, **69**, 169; Zts. Schiess. Spreng. 1906, **1**, 427.

motion of the gases, which pass out of a central opening. A. Bernutat¹ leads the acid through a series of chambers counter to the motion of hot gases. The Aktiebolaget Swedish Nitric Syndicate² cause the acid to flow through a vertical conduit packed with acid-proof material and heated externally, while a current of hot gas passes through the interior of the conduit.

'O. Proelss³ treats an acid of less than 63° Bé. with hot burner gases to concentrate it, and cause the deposition of impurities, a mixture of weak acid and nitrous vitriol being simultaneously treated with burner gases to secure an acid of medium strength, the deposits being dissolved by treatment with the last mentioned acid, and the gases from both operations being subjected to cool weak acid. It is difficult to see what advantage this process would have over the Glover tower.

L. Bouhon⁴ heats air from a blower in tubes and causes it to pass over the surface of the acid flowing down dimpled corrugated, rifled, or like plates. J. Skoglund⁵ injects a current of compressed air beneath the surface of a body of acid to cause a circulation and blow a portion into an upwardly directed spray, permitting the spray to fall back into the body of the acid. A current of hot gas is passed through the spray, the gas passing on being scrubbed.

T. Oliver⁶ subjects sulfuric acid containing metal sulfates to the action of an overlying current of hot gas, which agitates the liquid so as to prevent the formation of a crust. The solids settle out of the liquid, and are removed from below. T. Kilroy⁷ causes a descending, finely divided stream of sulfuric acid to meet an ascending stream of hot flue gases. The operation is con-

1. D. R. P. 281133, 1914; abst. C. A. 1915, **9**, 1834; Zts. ang. Chem. 1915, **28**, 83; Chem. Zentr. 1915, **86**, I, 176; Chem. Ztg. Rep. 1915, **39**, 11; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 111.

2. E. P. 10591, 1909; abst. C. A. 1910, **4**, 2554; J. S. C. I. 1910, **29**, 88.

3. U. S. P. 963174, 963175, 989537; abst. C. A. 1910, **4**, 2710; 1911, **5**, 2159.

4. E. P. 105935, 1916; abst. C. A. 1917, **11**, 2391; J. S. C. I. 1917, **36**, 645.

5. U. S. P. 1232109, 1917; E. P. 113551, 1917; Can. P. 179556, 1917; abst. C. A. 1916, **10**, 2394; 1918, **12**, 83, 1338. J. S. C. I. 1917, **36**, 925; 1918, **37**, 182-A. D. R. P. 310293, 1919; abst. Chem. Zentr. 1919, **90**, II, 337. Australian P. 4223, 1917.

6. U. S. P. 1240591; E. P. 105993, 1916; abst. C. A. 1917, **11**, 2391, 3393; J. S. C. I. 1916, **35**, 1015; 1917, **36**, 647.

7. U. S. P. 1211594, 1917; abst. J. S. C. I. 1917, **36**, 214.

ducted in a tower or series of towers, each composed of metallic sections with a packing of refractory material. The tower has a removable lead pan at the bottom and a distributing apparatus at the top. The acid is pumped from the bottom of one tower to the top of the next in the series, and the lead pans at the bottom are heated. O. Dieffenbach¹ proposes to separate the mixtures of acid vapor and steam produced by vaporization in a dephlegmating column.

A. Düron² proposes a modification of the Kessler apparatus, in which the currents of hot gas pass over the surface of the acid in parallel streams at right angles to the direction of motion of the acid. He claims that his apparatus is cheaper than Kessler's or the Gaillard tower, requiring less fuel than either, and less power than the Kessler, but more than the Gaillard.

S. Dreyfus and the Clayton Aniline Co.³ conduct the acid vapors without suction so that they come in contact with the acid to be concentrated, heating this to such a limited extent that only water or very weak acid is evolved. The operation is performed in a tower containing acid-proof packing, down which the acid trickles. If no weak acid vapors are evolved, it is difficult to see where those required in the process are obtained.

L. Stange⁴ describes a complicated apparatus of cast iron, containing acid, over the surface of which hot air is blown. The apparatus is cooled below, and consists of a receptacle for receiving the precipitate formed in the upper vessel. P. Pipereaut and Helbronner⁵ attempt to avoid the formation of fumes by passing the acid quietly in the same direction as the hot gas, in a series

1. F. P. 371685, 1906; abst. Chem. Ztg. Rep. 1907, **31**, 158; Mon. Sci. 1908, **69**, 80. D. R. P. 189863; abst. Zts. ang. Chem. 1908, **21**, 790; Chem. Zentr. 1907, **78**, II, 1953; Wag. Jahr. 1907, **53**, I, 336.
2. E. P. 344, 1913; D. R. P. 257559, 257573; abst. Chem. Ztg. 1913, **37**, 244. F. P. 453733, 453742; Aust. P. 62173, 1913; E. P. 104034, 1916; abst. J. S. C. I. 1917, **36**, 385; C. A. 1917, **11**, 1888. Belg. P. 253252, 1913. See also Chem. Ztg. 1914, **38**, 559. Zts. ang. Chem. 1914, **27**, I, 568; abst. C. A. 1915, **9**, 848. W. Strzoda, D. R. P. 272158, 1914; abst. C. A. 1914, **8**, 2608, 3706.
3. E. P. 788, 1902; abst. J. S. C. I. 1903, **22**, 26.
4. U. S. P. 837592; abst. C. A. 1907, **1**, 630. E. P. 91, 1907; abst. C. A. 1907, **1**, 2820; J. S. C. I. 1907, **26**, 967. D. R. P. 188901; abst. Zts. ang. Chem. 1908, **21**, 796; Chem. Zentr. 1907, **78**, II, 1283; Jahr. Chem. 1905-1908, I, 1616; Wag. Jahr. 1907, **53**, I, 337; Chem. Zts. 1907, **6**, No. 419. Aust. P. 33440, 1908. F. P. 373326, 1907; abst. Chem. Ztg. Rep. 1907, **31**, 324.
5. Mon. Sci. 1917, **84**, 265; abst. J. S. C. I. 1918, **37**, 6-A; C. A. 1918, **12**, 1108.

of twelve rectangular boxes. Gases at 1200° can be employed directly on acid of 53° Bé. I. Hechenbleikner¹ blows hot gases through tuyères on the surface of the acid, pass the vapors through a recuperator, and then through a filter. H. Jones² allows the acid to trickle over irregular surfaces, while hot gases pass over it. Other types of apparatus have been described by R. Sohlmann and W. Wilson,³ J. Harris,⁴ P. Pfannenschmidt and R. Moss.⁵

Other Methods of Concentration. H. Hegeler and N. Heinz⁶ concentrate the denitrated sulfuric acid in the lower part of the Glover tower by the addition of sulfur trioxide. The latter is said to be produced by mixing a portion of the nitrogen oxides liberated in the tower with sulfur dioxide. The Krell-Strzoda system⁷ uses concentrating tubes of acid-resisting iron⁸ enclosed in a shell of cast iron, the intermediate spaces being filled with acid-resisting cement. The concentrating tubes are arranged parallel on the slightly inclined bed of a furnace, and are connected at each end with a receiver for the distillate in such a manner that the acid passes from the first tube to the second, and so on through the series to the acid cooler and receiver. In a small plant of 6 tubes the production is "somewhat less than 0.9 ton" per 24 hours, of 97%-98% H₂SO₄. With "more than 6 tubes," the production is 0.9 ton. The fuel consumption is 4 cwt. per ton of acid.

In addition to the processes herein described, reference may be made to the patents of S. Littmann,⁹ R. Evers,¹⁰ Chance & Hunt,

1. U. S. P. 1264182, 1264509, 1918; abst. C. A. 1918, **12**, 1690; J. S. C. I. 1918, **37**, 414-A. Can. P. 191315, 1919; abst. C. A. 1919, **13**, 1905.
2. U. S. P. 1183207; abst. J. S. C. I. 1916, **35**, 736; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 179.
3. U. S. P. 1009196; abst. C. A. 1912, **6**, 277.
4. E. P. 7728, 1912; abst. C. A. 1913, **7**, 2999; J. S. C. I. 1913, **32**, 363; Chem. Ztg. Rep. 1913, **37**, 550.
5. E. P. 13642, 1914; abst. J. S. C. I. 1915, **34**, 798. See also G. Plath, Zts. ang. Chem. 1907, **20**, 444; abst. C. A. 1907, **1**, 1170. C. Negrier, U. S. P. 468891, 1892. Swed. P. 2830, 1890. F. P. 205239, 1890. Ital. P. 27843, 1890. E. P. 14022, 1890. Brazil P. 1052, 1890. D. R. P. 61321; abst. Wag. Jahr. 1892, **38**, 289. M. Faure and J. Kessler, U. S. P. 158924, 1875.
6. E. P. 2541, 1904; abst. J. S. C. I. 1904, **23**, 489.
7. W. Strzoda, Zts. ang. Chem. 1918, **31**, 185; abst. J. S. C. I. 1918, **37**, 688-A; C. A. 1919, **13**, 1127.
8. E. P. 26732, 1913; abst. C. A. 1915, **9**, 1230; J. S. C. I. 1914, **33**, 643.
9. D. R. P. 187253, 1906; abst. J. S. C. I. 1908, **27**, 502; Zts. ang. Chem. 1908, **21**, 795; C. A. 1908, **2**, 576, 600.
10. D. R. P. 178369; abst. C. A. 1907, **1**, 1207; Chem. Centr. 1906, **77**,

Ltd.,¹ W. T. Clough,² D. Ashworth and R. Eaton,³ J. Hughes and J. Hitchcock,⁴ P. Marcelin and J. Saunders,⁵ A. Ungerer,⁶ J. Smith and J. Savage,⁷ R. Küch,⁸ G. Hagemann,⁹ J. Saunders,¹⁰ R. Wallace,¹¹ J. Gridley,¹² C. Kolbe and T. Lindfors,¹³ F. Kalbfleisch,¹⁴ J. Hesch,¹⁵ W. West,¹⁶ S. McDougall,¹⁷ M. Walsh,¹⁸ M. Willett,¹⁹ C. Battsch,²⁰ K. Sundström,²¹ J. Herreshoff,²² H. Pischon and R. Pfennig,²³ E. Nation,²⁴ O. Guttman,²⁵ H. Howard,²⁶ W. Wolters,²⁷ J. Falding,²⁸ D. Cardozo,²⁹ E. Dyson,³⁰ G. Krell,³¹ J. Ackerson,³² R. Penniman,³³ J. Patten,³⁴ W. Quinan,³⁵ L. Stange,³⁶ G. de Bri-

II, 1668; *Jahr. Chem.* 1905-1908, I, 1615; *Chem. Ztg. Rep.* 1906, **30**, 387; *Wag. Jahr.* 1906, **52**, I, 391; *Mon. Sci.* 1908, **69**, 169; *Zts. Schiess. Spreng.* 1906, **1**, 427.

1. E. P. 126320; abst. *J. S. C. I.* 1919, **38**, 498-A; *C. A.* 1919, **13**, 2258.
2. U. S. P. 15222, 1856; 127957, 1872.
3. U. S. P. 62919, 1867; 78352, 1868.
4. U. S. P. 65227, 1867; 339552, 1886.
5. U. S. P. 77826, 1868.
6. U. S. P. 146728, 1874.
7. U. S. P. 41647, 1864.
8. U. S. P. 474527, 1892; abst. *J. A. C. S.* 1892, **14**, 140.
9. U. S. P. 165567, 1875.
10. U. S. P. 171049, 1875.
11. U. S. P. 196957, 1877.
12. U. S. P. 240248, 1881; 265495, 1882; abst. *J. A. C. S.* 1881, **3**, 69; *Wag. Jahr.* 1883, **29**, 266.
13. U. S. P. 246396, 1881; abst. *J. A. C. S.* 1881, **3**, 165.
14. U. S. P. 267221, 1882.
15. U. S. P. 275041, 1883.
16. U. S. P. 280425, 1883. E. P. 1651, 1883; abst. *J. S. C. I.* 1884, **3**, 30.
17. U. S. P. 289293, 1883; abst. *Wag. Jahr.* 1884, **30**, 299.
18. U. S. P. 291821, 1884; abst. *J. A. C. S.* 1884, **6**, 52; *Wag. Jahr.* 1884, **30**, 299.
19. U. S. P. 301033, 1884; abst. *J. A. C. S.* 1884, **6**, 294.
20. U. S. P. 318682, 1885; abst. *J. A. C. S.* 1885, **7**, 155.
21. U. S. P. 349414, 1886; abst. *J. A. C. S.* 1886, **8**, 237.
22. U. S. P. 357528, 369790, 1887; abst. *J. A. C. S.* 1887, **9**, 39.
23. U. S. P. 374268, 1887; abst. *J. A. C. S.* 1887, **9**, 226.
24. U. S. P. 395505, 1889.
25. U. S. P. 505520, 1893; 627749, 1899; abst. *J. A. C. S.* 1893, **15**, 503.
26. U. S. P. 509664, 1893; abst. *J. A. C. S.* 1893, **15**, 711.
27. U. S. P. 514983, 1894. Cf. D. R. P. 15639; abst. *J. S. C. I.* 1882, **1**, 26; *Wag. Jahr.* 1882, **28**, 264; *Mon. Sci.* 1882, **24**, 324.
28. U. S. P. 541041, 1895. D. R. P. 76691; abst. *Wag. Jahr.* 1894, **40**, 449; *Zts. ang. Chem.* 1894, **7**, 566; *Jahr. Chem.* 1894, **47**, 407; *Ber.* 1894, **27**, 945.
29. U. S. P. 542626, 1895.
30. U. S. P. 548303, 1895.
31. U. S. P. 549138, 1895.
32. U. S. P. 453801, 1891; abst. *J. A. C. S.* 1891, **13**, 186.
33. U. S. P. 469439, 1892; abst. *J. A. C. S.* 1892, **14**, 41.
34. U. S. P. 676663, 676664, 1901; abst. *J. A. C. S.* 1902, **24**, 113.
35. U. S. P. 699011, 1902; abst. *Mon. Sci.* 1902, **58**, 183; *Chem. Zts.* 1903, **2**, 8.
36. U. S. P. 827592, 1906; abst. *Chem. Ztg. Rep.* 1907, **31**, 72; *Mon.*

ailles,¹ T. Oliver,² Frankfurter Maschinenbau A. G.,³ and others.⁴

Electrostatic Precipitation. One of the most important modern adjuncts to the concentration of sulfuric acid is electrostatic precipitation. A gas may become a conductor of electricity in various ways, such as by exposure to ultraviolet light, X-rays, and radium, and is then said to be ionized. Its molecules carry positive and negative electric charges. If an electrostatic field is imposed on the gas, the ions move toward the electrodes of opposite sign, and are discharged on impinging on them. If the electrodes are charged to a sufficiently high potential they may act as ionizing agents, as well as causing the ions to move. The gaseous ions moving away from the electrodes impinge on solid or liquid particles in their path, and charge them. The charged particles now travel to the electrodes of opposite sign, where they are deposited. The rate of production of ions depends also on the shape of the electrodes, pointed or narrow electrodes being more effective than flat plates.

These are the principles of the electrostatic precipitator.

Sci. 1907, **67**, 113. See also U. S. P. 986846; abst. C. A. 1911, **5**, 1978. F. Moore and J. Hall, abst. C. A. 1911, **5**, 1978. W. Bate and F. Orme, E. P. 25790, 1902; abst. J. S. C. I. 1903, **22**, 212. F. Brown and United Alkali Co., E. P. 14321, 1915; abst. 1917, **36**, 1227. A. Gellen, Aust. P. 60565, 1912. A. Nobel, D. R. P. 10149, 1880; abst. J. A. C. S. 1880, **2**, 355. Soc. Le Nitrogene, Aust. P. 49481, 1911. Chem. Fabrik Griesheim-Elektron, Aust. P. 28968, 1907; Aust. P. 26684, 1906; D. R. P. 174736. G. Krell, Aust. P. 21305, 1905. H. Lemaitre, F. P. 357555; abst. C. A. 1907, **1**, 630. See also Chem. News, 1861, **3**, 4; 1869, **20**, 107; 1871, **23**, 167; 1871, **24**, 82, 106; 1872, **25**, 215; 1872, **26**, 174; 1873, **27**, 185; 1876, **33**, 95; 1877, **36**, 111; 1879, **40**, 228; 1892, **65**, 227; 1894, **70**, 318. Cumming, Romanes and Walker, E. P. Appl. 17306, 1915. C. Kaesmacher, F. P. 386783, 1908; abst. J. S. C. I. 1908, **27**, 749.

1. Swiss P. 45639, 1908.

2. U. S. P. 1195075; abst. Chem. App. 1919, **6**, 66; C. A. 1919, **13**, 2974.

3. Swiss P. 70624; see also A. Bernutat, D. R. P. 281133; Fab. de Soie Artificielle de Tubize, E. P. 10386, 1915; D. R. P. 303123; U. S. P. 1323847, 1919; abst. J. S. C. I. 1916, **35**, 537; 1920, **39**, 64-A.

4. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, D. R. P. 284053; J. Skoglund, D. R. P. 310293; O. Brünler, D. R. P. 283790; abst. Chem. App. 1919, **6**, 66; C. A. 1919, **13**, 2974. J. Loftus, U. S. P. 60759, 1867. P. Marcollin and J. Saunders, U. S. P. 77202, 1868. A. Newman, U. S. P. 1294525; abst. C. A. 1919, **13**, 1132; J. S. C. I. 1919, **38**, 361-A. F. Perrin, E. P. 118095; abst. J. S. C. I. 1919, **38**, 518-A; U. S. P. 1301598; abst. C. A. 1919, **13**, 1904. J. Patten, U. S. P. 1294827; abst. J. S. C. I. 1919, **38**, 361-A; C. A. 1919, **13**, 1132. J. Perrin and J. Saunders, U. S. P. 78760, 1868. H. Jander, U. S. P. 1321210, 1919; abst. J. S. C. I. 1920, **39**, 20-A; C. A. 1919, **13**, 209. Southern Electro-Chemical Co., Can. P. 191314, 191315, 1920. Soc. Union des Fabricants d'Acide Sulfurique de France, F. P. 493692, 1916; abst. Chim. Ind. 1920, **3**, 204.

They have been well known for a number of years, and the method was used by Lodge and others for precipitating fogs. It has been shown as a lecture experiment for some time. It is, therefore, quite correct to refer to it as the Cottrell method, because Cottrell was the first to apply the method on a large scale, and to devise apparatus whereby the necessary potentials could be applied. It has been said that many of the principles embodied in his apparatus are but amplifications of ideas first promulgated by Lodge, and perfected by Cottrell.

It is usual to make one electrode in the form of a wire or point, and the other a surface, either a flat plate, or a cylinder surrounding the wire. Both tube and plate treaters have been used. The latter is better adapted to the condensation of sulfuric acid mists produced in the concentration of the acid.

A word may be said about these mists. If sulfuric acid is boiled in a retort, and the fumes led into a receiver, they condense to liquid acid without forming appreciable mist. No difficulty is experienced in causing such vapors to condense. But if the acid is evaporated in a current of air or other indifferent gas, an entirely different state of affairs results. A dense fog or fume is produced, which will not condense on simple cooling, but will do so if caused to impinge on surfaces, say, by filtering the fog at a fairly high speed through a coke filter, or passing it through capillary tubes. The mist is not deposited by passing the fog through water, but is easily absorbed if passed through concentrated sulfuric acid. These peculiar properties have not yet been adequately explained; the explanation given by A. Smith (*Inorganic Chemistry*, 1919, p. 429) would appear to be incorrect. Partington reports that similar mists are formed in condensing nitrous fumes in water, and in passing them through solutions of ammonia. He finds in the latter case that if the fumes of NH_4NO_3 are passed through concentrated sulfuric acid, they at once deposit solid in the tube *after* passing through the acid, but not in the acid itself. Again, if a mixture of air and HCl is blown through conc. ammonia solution, a fog of NH_4Cl is produced which settles only with great difficulty, whereas if a mixture of NH_3 and air is blown through conc. HCl a fog of NH_4Cl is formed which readily settles.

The peculiar character of these mists has led technical chem-

ists to regard them as consisting of droplets existing in a peculiar state which they call *vesicular*. It is supposed that the droplets are hollow, and deport themselves like little India rubber balls, rebounding from surfaces with which they come in contact. There is no evidence for this hypothesis, and a more reasonable explanation seems to be that the droplets are not hollow, but that they are kept from coalescing by surface tension, and by the repulsive action of electric charges residing upon them. Further investigation of the structure and properties of mists is, however, required.

A. Heimrod and H. Egbert¹ report that, in precipitating sulfuric acid fogs, a tubular precipitator is used. In the plant described, 3000 cu. ft. of gas per minute at 57° are treated from three tower concentrators, yielding 50 tons of 66° Bé. acid per 24 hours. In that time 3000 lbs. of 18° Bé. acid are recovered from the mists. A potential of 75,000 volts is employed, with a power consumption of 3½ K. W. Another unit, similarly equipped electrically, of 12 tubes each 12 in. by 15 ft., treats 2500 cu. ft. of gas per min. at 93° from 2 towers producing 40 tons of 66° Bé. acid per 24 hours, and 3500 lbs. of 33° Bé. acid are recovered. One of the largest installations treats 30,000 cu. ft. of gas per min. at 82° from 22 cascade concentrators, each producing 10 tons of 66° Bé. acid per 24 hours. Four units, each of 12 tubes as above, are employed, and 25 tons of 45° Bé. acid are recovered per 24 hours. It will be noted that this corresponds with a loss of acid from the cascades of 11%, which confirms the figures quoted in that section. This loss may be exceeded in some plants, and may rise to 20%. The induced draft is provided by fans, which are more satisfactory than steam injectors.

C. Schiffner² also gives results of the method, and K. Shiga³ quotes the results obtained in American factories, with a bibliography of the process.

A Cottrell plant was installed at Queen's Ferry, England, to deal with the fumes from the Gaillard towers in use there. The acid recovered amounted to 30 tons of 51% H₂SO₄ per day,

1. Chem. Met. Eng. 1918, **19**, 309; abst. J. S. C. I. 1918, **37**, 729-A; C. A. 1919, **13**, 501. G. Moss, J. S. C. I. 1918, **37**, 68-T.

2. Metall u. Erz. 1914, **11**, 257; abst. Chem. Ztg. Rep. 1914, **38**, 383; C. A. 1914, **8**, 2904. See also E. Streiff, Belg. P. 150320, 1900. E. Thum, Chem. Met. Eng. 1919, **20**, 59; abst. J. S. C. I. 1919, **38**, 163-A.

3. J. Chem. Ind. Japan, 1918, **21**, 136; abst. C. A. 1918, **12**, 1859.

from a total of 420 tons H_2SO_4 charged to the towers as 67.5% H_2SO_4 . This represents a recovery of 3%–3.5%. About 1% of the acid was lost through the stack. These figures show in a striking manner the much lower fume loss from Gaillard towers than from cascades. The fan used for aspirating the gases used 80 K. W. The average voltage of the treaters was 73,600, and the power consumption 26 K. W.

The treater at Queen's Ferry was of the plate type, the concentration plant consisting of 2 houses of 8 Gaillards, the fumes being led through a common lead flue to the 4 treater chambers. From the treaters the gases again united in a common flue from which two brick flues conveyed them to the stack. Each treater is 30 ft. $1\frac{1}{2}$ in. long, 7 ft. 6 in. wide, and 8 ft. 6 in. high, all inside dimensions. It was built of acid-proof bricks, supported on a concrete foundation covered with acid-proof bricks and lead, the bottom of the treater being formed of a lead tray. The lead plates forming one set of electrodes were supported from lead covered mild steel bars, and the rods of antimonial lead forming the other set of electrodes hang between them. All the horizontal supporting bars were insulated on brickwork chambers built at the side of the treaters. The lead plates were of 8-lb. lead, 2 ft. wide and 8 ft. 5 in. long. The rods were 7 ft. $1\frac{3}{4}$ in. long, of cruciform section, the four wings being 1 in. long and $\frac{1}{8}$ – $\frac{3}{16}$ in. thick. The edges were sharpened as finely as possible to promote discharge. They were burned in sets of 8 to lead covered steel bars, there being 18 bars to each chamber, or 144 rods. 8 rows of 8 plates were hung on each side of the rods.

The electrical apparatus was of the usual type, containing high tension transformers, with rotary switch rectifiers. Unidirectional current must be used. The rods were negative, the plates and positive poles were earthed. The normal temperature of the gases entering the treaters was 85°–90°, corresponding with a fan temperature of 100°. The gases left the treaters at 10°–15° below the entrance temperature.

The chief objection to the Cottrell process is its high cost compared with coke filters. Its efficiency has been demonstrated to be of the order of 80%.¹ H. Welch² uses an electrical precip-

¹ The Cottrell process for the electrical precipitation of suspended particles is covered by the following patents: "Manufacture of sulfuric acid," U. S. P. 866843, 1907; abst. Mon. Sci. 1908, 69, 49; J. S. C. I. 1907,

itation method for recovering waste acid from the manufacture of nitrocellulose and nitroglycerol.

The Gilchrist Concentrator. At the Queen's Ferry Plant, the weak sulfuric acid is first pumped by 8" Impellor Twin Kynock pumps from the lead vats which receive the residual acid from the stills and the Grillo scrubber acid, through a 3" main, to two lead storage tanks 8' 4" diam. by 3' 6" deep. Each tower is fed from an overhead lead-lined feed tank, 10' x 15' x 4' 6", into which the acid is raised, through a lift of 73½ feet, either by 4 Kestner elevators, each capable of raising 3 tons per hour, or by one of three 2" belt-driven Douglas pumps. The acid is fed by siphon feed from these tanks to three distributing launders running across the top of the tower. The acid overflows from 8 lips on each side of these into lead funnels leading down to the lutes in the lead cover.

The acid is concentrated as it flows through the packing of the tower and delivers into a satux pan, where further concentration is effected, being finally delivered through coolers to the storage coolers as concentrated acid. The gases are led from the main tower through a quartz packed scrubber, to a 21" Kestner fan, and thence to the stack. The Cottrell precipitating plant is to be operated in conjunction with this.

There have been installed two independent units, each capable of producing 70 short tons of 93.5% H_2SO_4 from 65.5% acid, or 35 short tons of 97% H_2SO_4 from 65.5% acid, using in both cases 162,000,000 B. T. U.'s per 24 hours, or approximately one million feet of producer gas.

The furnace comprizes a firebrick structure sheathed in steel, 26, 1138. Australian P. 9734, 1907. "Apparatus for separating sulfuric acid," U. S. P. 866844, 1907; abst. J. S. C. I. 1907, 26, 1138. "Art of separating suspended particles from gaseous bodies," U. S. P. 895729, 1908. "Effecting interchange of electrical charges between solid conductors and gases," U. S. P. 945917. "Filtering medium and process of making the same," U. S. P. 1060065, 1913; abst. C. A. 1913, 7, 2038. "Purification of gases," U. S. P. 1016476, 1909; abst. C. A. 1912, 6, 796. "Apparatus for separating suspended particles from gaseous bodies," U. S. P. 1035422. "Method of discharge of electricity into gases," U. S. P. 1067974, 1913; abst. C. A. 1913, 7, 2907. See also J. Ind. Eng. Chem. 1911, 3, 542. Proc. Am. Min. Cong. 1916. J. Ind. Eng. Chem. 1919, 11, 148, 154; J. S. C. I. 1919, 38, 121-T. E. P. 21147, 1907; abst. C. A. 1908, 2, 2979; J. S. C. I. 1908, 27, 404. F. P. 382179, 1907; abst. Mon. Sci. 1909, 71, 102. Cf. L. Bradley, U. S. P. 1284175; abst. C. A. 1919, 13, 166; J. S. C. I. 1919, 38, 74-A. 2. U. S. P. 1289984; abst. C. A. 1919, 13, 773. E. P. 134593, 1918; abst. J. S. C. I. 1920, 39, 20-A. Can. P. 194775, 194776, 194777; abst. C. A. 1920, 14, 601.

the gas being led from the main producer flues to the furnace by two gas flues, 2' x 3', controlled by valves, and enters the combustion chamber through any of four 6" x 12" gas ports, expanding to 12" x 18" after admixture with the primary air. The admittance of the air for combustion is controlled by mushroom ports at the front of the furnace. The combustion chamber measures 8' x 11' x 5' 3", surmounted by a false arch, over which the secondary air is admitted. The products of combustion then enter an upcast 8' x 4' 6" x 11', filled with checker brickwork, and are delivered to the satux by a cross connecting flue, 4' 6" x 5'. The combustion chamber is equipped with the necessary explosion doors and peep holes.

The satux is 37' 7 $\frac{1}{2}$ " long by 9' wide, inside dimensions, the whole structure being raised on a concrete foundation 9' above the ground level, so as to give the necessary gravity flow to coolers and tanks. The concrete is protected by 6-lb. lead sheets. The saturator consists of a pan 18" deep, of 20-lb. lead, lined with 3 layers of acid-proof tile, set in silicate cement. The firebrick arch to the satux is fitted with 4 baffle arches, which deflect the hot gases from the furnace down on to the surface of the acid. The whole structure is bound with the necessary brick stays, the brickwork containing cavities to take up expansion. The sludge outlets and run-offs are fixed so that a depth of 7" of acid remains in the satux.

A certain amount of circulation of the acid in the satux is assured by two 28' Narki spigot and socket pipes, connected to the compressed air main, and having eighth-inch perforations at distances of 6" apart. The concentrated acid overflows from the satux into a collecting brick-lined launder, from which it delivers to any of five lead coolers through a Narki run-off pipe.

The acid leaves the satux at a temperature of 250°, each cooler being capable of cooling 100 tons daily from this temperature down to 35°. Each cooler is 3' 5" in diam. x 4' 4 $\frac{1}{2}$ " deep, of 16-lb. lead, and fitted with a water jacket for the upper 30". There are provided 3 cooling coils of 1 $\frac{1}{2}$ " lead pipe, consisting of 14 turns, each 15", 22" and 29" in diameter. The base of the main tower is contained in the same lead pan as the satux, and is 11' square (inside measurement) and 47' 3" high. The base is lined with acid-proof tile as in the satux, the packing of

the tower resting on 7 arches, sprung from the sides of the tower.

The tower is constructed of acid-proof bricks, with special American cement, the walls being 1' 6" thick, with 4 1/2" inner wall, lined with acid-resisting tile extending to a height of 14'. The walls are bonded every 4', vertically and horizontally. The tower is tied by rods and corner angles each 3' of its entire height.

The gases pass from the tower into the scrubber by a 36" off-take of 12-lb. lead, stiffened by lead-covered iron bands. This contains a 60 Gaillard spray, through which water is sprayed to cool the gases. It should be remembered, however, the water spray is uneconomical in that it increases the concentration load, while attempts to spray weak acid into the off-take instead of water has proven quite successful.

The scrubber rests on a 15-lb. lead pan, and is 31' 6" high with 18" walls of acid-resisting brick, with a 4 1/2" inner wall rising to a height of 13' 3". A lining of 1 1/2" tile is carried right up to the top of the scrubber. The internal cross-section is 15' 1 1/2" x 12' 10 1/2" at the base, increasing to 15' 10 1/2" x 13' 7 1/2" above the top of the inner wall. The structure is bound by tie-rods and corner angles as in the main tower.

The packing is bound on checker brick work, so arranged as to give a free gas exit to the fan, and consists of the required layers of 10" and 6" quartz to carry the main filling of 2" quartz, the total packing weighing about 300 tons. The 60 Gaillard sprays are fixed into the top of the dome, fed by weak acid from the same feed pipe as the spray on the main tower off-take. The scrubber acid is delivered to the scrubber acid tank through 24 acid ports, each 4 1/2" x 3", issuing into an external launder.

Each unit is fitted with one 21" Kestner high pressure fan, of the same type as used in the Gaillard towers. The fans deliver through a 21" lead main into the Cottrell flue, 2' x 2' 6", this being so graded as to drain any condensed acid back to the scrubber launder. The fumes pass for further scrubbing into a Cottrell chamber and thence into the stack.

* It is understood that the most serious trouble experienced in connection with this plant at Queen's Ferry has been the excessive wear and tear on the base of the tower and saturex. The temperature of the acid in the saturex causes the tiles to expand and lift, thus forming channel ways through which the acid percolates

to the lead base, which, in consequence, in a short time, is eaten through, and the concrete foundation attacked. Whenever a leakage of this nature appears it necessitates taking up the whole of the tiling and renewing the entire or a major portion of the lead work.

Careful control of the temperatures of the furnace and the acid in the saturex decreases the trouble, but does not entirely obviate it. The sludging up of the units presents another difficulty, for the sludge in the feed acid settles in the saturex, and is sufficient in amount to necessitate sludging out each unit once per month, the whole of the saturex, by that time, being full of sludge. Even when no repairs are indicated, the unit has to be thoroughly cooled down and drained, before the saturex can be washed out. The definite opinion has been formed that this type of concentrator cannot be compared with a Gaillard tower, properly constructed and operated.

At the British Acetones plant at Toronto, Can.,¹ two 30-ton Gilchrist towers were installed to reconcentrate the sulfuric acid diluted in the regular plant operation. The coolers for the concentrators were located below the main operating floor. The method of taking Baumé readings hourly by dipping samples from the discharge pipe to the cooler and taking hydrometer readings from the dippers had disadvantages in that acid was splashed on the operators' clothes, and hydrometer breakages were high. The original article gives details of a simple, continuous sampling device which was evolved, and eliminated the troubles above referred to.

Recent Advancement. In connection with the subject of contact masses (see pp. 915, 1108-1120) N. Sulzberger² reduces

1. S. Ionides, *Chem. Met. Eng.* 1919, **20**, 38; abst. C. A. 1919, **13**, 904.
2. U. S. P. 1338700, 1920; abst. J. S. C. I. 1920, **39**, 437-A. Additional information on sulfur trioxide and contact processes will be found by consulting Audianne, E. P. Appl. 16731, 1920; abst. J. S. C. I. 1920, **39**, 504-A; E. P. 142522, 1918; abst. J. S. C. I. 1920, **39**, 487-A. *Farbenfabr. vorm. F. Bayer & Co.*, D. R. P. Ann. F.34801, 1912; Span. P. 55090, 1913; Belg. P. 258157, 258963; Canadian Explosives Ltd., Can. P. 137540, 1911. P. Cantilena, Ital. P. 135019, 1913. P. Farup, D. R. P. Ann. F.35006; Belg. P. 254287. Grasselli Chem. Co. and P. Lihme, Can. P. 176011, 1917. R. Knietseh, U. S. P. 794512, 1905. R. Knietseh and M. Scharff, U. S. P. 782782, 1905. C. Krauss and R. von Berneck, U. S. P. 720309, 1903. H. Potts, U. S. P. 1335257; abst. C. A. 1920, **14**, 1599; J. S. C. I. 1920, **39**, 403-A. W. Richardson, U. S. P. 1338698, 1920; abst. J. S. C. I. 1920, **39**, 437-A. W. Schuck, E. P. 142576, 1919. G. Vortmann, D. R. P. 316858; abst. J. S.

a metallic borate possessing catalytic activity, sufficient of the borate radical being present to serve as an effective carrier of the catalytic metal after reduction, or,¹ porous ceramic material, preferably in the form of small tubes with projecting rims, is employed by V. Zieren as a support for contact substances. In another process,² the catalyst is intimately incorporated with

C. I. 1920, **39**, 403-A; Chem. Zentr. 1920, **91**, II, 370. F. Washburn, Can. P. 165773, 1915; 179101, 1917. See also Can. P. 142874, 143341, 143602, 143848, 144760, 144478, 144479, 144895, 145058, 145059, 145824, 145430.

1. D. R. P. 317979, 1917; abst. J. S. C. I. 1920, **39**, 355-A. Recent processes for the preparation and utilization of SO₂ are: J. Blanc, Aust. P. 60432. Chem. Fabr. vor. Weiler-Ter Meer, D. R. P. 307121, 1918; abst. J. S. C. I. 1920, **39**, 295-A; Chem. Tech. Übers. 1920, **44**, 111. N. Christensen, U. S. P. 1341734; abst. C. A. 1920, **14**, 2242. Deutsche Petroleum A.-G., D. R. P. Anm. D-35111, 1918. L. Diehl, E. P. 139172, 139173, 1920. E. Dohet, E. P. 7892, 1913. V. Erchenbrecher, D. R. P. 307752, 1917; abst. J. S. C. I. 1920, **39**, 406-A; Chem. Zentr. 1920, **91**, II, 484. E. Espeuhahn, Can. P. 195152, 1919. A. Eustis, U. S. P. 1341114, 1341115; abst. J. S. C. I. 1920, **39**, 517-A; Can. P. 201362, 1920. F. Eustis, Can. P. 175646, 187105, 1918. J. Fairrie, E. P. 144142, 1919; abst. J. S. C. I. 1920, **39**, 548-A. E. Freese, Wochbl. Papierfabr. 1920, **51**, 861; abst. C. A. 1920, **14**, 2119. A. Guiselin, F. P. 442259, 1912. D. Hemt, Russ. P. Appl. 54465, 1912. D. Hunt, D. R. P. 266518, 1912. J. Jones, D. R. P. 262393; Can. P. 141243, 1912. H. Lyon, U. S. P. 1337561, 1920; abst. J. S. C. I. 1920, **39**, 488-A. Metallbank u. Metallurg. Ges., D. R. P. 300061, 1916. J. Meyer, Ber. 1920, **53**, 77-B; abst. J. S. C. I. 1920, **39**, 229-A. F. Miles and J. Fenton, J. C. S. 1920, **117**, 59; abst. J. S. C. I. 1920, **39**, 229-A; C. A. 1920, **14**, 1771; Chem. Zentr. 1920, **91**, I, 813. H. Moore and G. Richter, Can. P. 153444, 1914; 200396, 1920. H. Niedenfür, D. R. P. Anm. N-11703, N-11727, 1910. G. Oddo, Ital. P. 114024. J. Parent, Ital. P. 121670, 1911. D. Peniakoff, Ital. P. 128341. C. Renwick, D. R. P. Anm. R-32345, 1911. E. Rossiter, Can. P. 146935, 1913. H. Stout, Can. P. 106941. E. Sutcliffe, Belg. P. 258608, 1913. J. Terwelp, D. R. P. 300035, 1917; abst. J. S. C. I. 1920, **39**, 489-A. M. Trautz, D. R. P. Anm. T-23458, 1919. F. Voltz Sohn, D. R. G. M. 574423, 1913.

2. Nitrogen Ltd., D. R. P. 312726, 1912; abst. J. S. C. I. 1920, **39**, 393-A. For recent data on obtaining sulfur from pyrites and other ores, sulfates, sulfides and SO₂, see Aktiebolaget Kolloid, Aust. P. Anm. 2572, 1913; Ital. P. 132530; Swed. P. 35040, 1912. A.-G. f. Anilinfabrikation, D. R. P. 300715, 1916; abst. J. S. C. I. 1920, **39**, 406-A; Chem. Zentr. 1920, **91**, II, 484. Badische Anilin- u. Soda-Fabrik, D. R. P. 302433; abst. Chem. Zentr. 1920, **91**, II, 434; J. S. C. I. 1920, **39**, 365-A; D. R. P. 305123, 1917; abst. J. S. C. I. 1920, **39**, 295-A. E. Banes, Ital. P. 117773, 1911. G. de Bechi and S. Bornett, Belg. P. 256428. E. Bracq, U. S. P. 1335271, 1918 (see p. 1076); abst. J. S. C. I. 1920, **39**, 365-A. British Sulphur Co., Belg. P. 258764, 1913; Hung. P. Anm. B-6588, 1913; Norw. P. 30789, 1913. L. Bishnell and H. Clark, J. Ind. Eng. Chem. 1920, **12**, 485; abst. J. S. C. I. 1920, **39**, 447-A. Chance & Hunt, Ltd., D. R. P. 263389; Aust. P. Anm. 10421, 1912. Chem. Fabrik Rhenania and F. Prohahn, D. R. P. 298844, 1916. Chem. Ind. A.-G. and F. Wolf, D. R. P. Anm. C-19581, 1910. E. Ciselet and C. Deguide, Belg. P. 256175. T. Clayton, E. P. 141661, 1919. C. Stevens, Can. P. 195076, 1919. M. Comas y Gusi, E. P. 20758, 1912. H. and M. Davis, J. Ind. Eng. Chem. 1920, **12**, 479; abst. J. S. C. I. 1920, **39**, 516-A. W. Feld, D. R. P. Anm. F-33663, F-34066; Ital. P. 132255, 1913. H. Fischer, Chem. Ztg. 1920, **44**, 239; abst. Chem. Zentr. 1920, **91**,

hydraulic cement, and the mass allowed to set without pressure, the contact mass being composed of cement 85%, copper oxide 10%, alumina 5%. P. Haeseler¹ reacts with a reducible selenium compound containing oxygen, while C. Ellis² advocates an active basic tin compound and voluminous chromium oxide. The General Electric Co.³ specify "fibrox" (silicon oxycarbide) as a

II, 754; T. Forland, F. P. 456063, S. Gancelin, Ital. P. 127941, General Chem. Co., Can. P. 140321, 140322, 1912; 166940, 166941, 1916. H. Gouthiere & Cie. and P. Ducancel, Hung. P. Appl. G-3378, 1911. W. Hall, Port. P. 8859, 1913; Can. P. 162082, 162393, 162516, 1915. J. Hood, U. S. P. 1331645, 1331646; C. A. 1920, **14**, 1196; J. S. C. I. 1920, **39**, 295-A; E. P. 140844, 1918; abst. J. S. C. I. 1920, **39**, 365-A; C. A. 1920, **14**, 2242. Imbert Process Co., Belg. P. 240518, 1911. O. Kaselitz, Zts. ang. Chem. 1920, **33**, 49; abst. J. S. C. I. 1920, **39**, 265-A; C. A. 1920, **14**, 2056. J. Kiernayer and Hannoverische Kaliwerke A.-G., D. R. P. 310072, 1916; abst. J. S. C. I. 1920, **39**, 406-A. W. Lamoreaux, Can. P. 162040, 1915; 166632, 169556, 1916. F. Panzera, Ital. P. 117562. P. Patti, Ital. P. 114822, 1911. M. Raffo, Ital. P. 132127. M. Ruthenburg, E. P. 29030, 1912. L. di Luigi, Aust. P. Ann. 4912, 1910. H. Starr, U. S. P. 1065319. The Thiogen Co., Can. P. 147882, 148140, 1913; 166284, 1915; Ital. P. 132523, 1913; D. R. P. Ann. T-17991, 1912; Hung. P. Appl. T-2215. Thomsen Chem. Co., E. P. 435197, 1911; Can. P. 150891, 1913. F. Beeraft, A. Genter and United Filters Corp., U. S. P. 1332537, 1920; abst. J. S. C. I. 1920, **39**, 335-A. W. Clifford and T. Green and United Filters Corp., U. S. P. 1332542, 1920; abst. J. S. C. I. 1920, **39**, 365-A. F. Weeren, D. R. P. 301712, 1915; abst. J. S. C. I. 1920, **39**, 335-A.

1. U. S. P. 1341462, 1920; abst. J. S. C. I. 1920, **39**, 516-A; C. A. 1920, **14**, 2240.

2. Can. P. 177145, 1917; 186962, 1918; U. S. P. 1335161, 1920; abst. J. S. C. I. 1920, **39**, 355-A.

3. U. S. P. 1299641, 1919; abst. J. S. C. I. 1919, **38**, 415-A; E. P. 140011, 1919; abst. J. S. C. I. 1920, **39**, 323-A. For additional data on the chamber and allied processes, see A. Aita, Giorn. chim. ind. 1920, **2**, 1; abst. C. A. 1920, **14**, 1135. A.-G. f. Bergbau, Blei u. Zinkfabrikation in Westfalen, D. R. P. Ann. A-20738, 1911; abst. Chem. Ztg. 1912, **36**, 786. A. Burkhardt, D. R. P. Ann. B-68102, B-65372; Belg. P. 252160; abst. Chem. Ztg. 1913, **37**, 472, 670. Chem. Fabrik Griesheim-Elektron, D. R. P. 305122, 1917; abst. J. S. C. I. 1920, **39**, 393-A. N. Dekker, Can. P. 167446, 1916. B. Dirks, D. R. P. 301791; abst. J. S. C. I. 1920, **39**, 266-A. E. DuPont de Nemours Powder Co., Can. P. 134525, 1910. Harkortsche Bergwerke u. Chem. Fabriken zu Schwelen u. Harkorten, D. R. P. Ann. B-70709; abst. Chem. Ztg. 1913, **37**, 891. E. Hartman, Ges., D. R. P. Ann. H-59900; abst. Chem. Ztg. 1913, **37**, 616; Belg. P. 258631, 1913. E. Hoefling, D. R. P. Ann. H-57552. H. Ising, D. R. P. Ann. I 15442. P. Jannasch and E. Alberts, D. R. P. 318221; abst. J. S. C. I. 1920, **39**, 403-A. O. Jensen, Can. P. 200430, 1920. T. Kalinowsky, D. R. P. Ann. K-52385. Kaltenbach, Chim. et Ind. 1920, **3**, 407; abst. J. S. C. I. 1920, **39**, 484-A. E. Larison, U. S. P. 1342024; abst. C. A. 1920, **14**, 2240; J. S. C. I. 1920, **39**, 363-A. J. Leitch, Can. 173462, 1916. R. Lessing, E. P. 139880; abst. J. S. C. I. 1920, **39**, 321-A. Z. Littmann, Aust. P. Ann. 3610, 1912; D. R. P. Ann. L-36372; Belg. P. 260066, 1913. J. Lütjens, D. R. P. Ann. L-33500, 1911. G. Lüttgen, D. R. P. Ann. L-34366. R. Moritz, Belg. P. 250781. Det Norske Aktieselskab f. Elektrokemisk Industri, Can. P. 151615, 1913. J. Oliphant, Chem. Met. Eng. 1920, **22**, 408; abst. C. A. 1920, **14**, 1413. C. Opl und Erste Oesterr. Sodafabrik, U. S. P. 1012387, 1909. E. Packard &

suitable support for other catalysts, especially for as platinum.

In an amplification of the "heat-rise" method of testing sulfuric acid and oleum as described by H. Howard,¹ R. Curtis and F. Miles² (see p. 1127) have described a method claimed to be unusually accurate.

Co., Norw. P. Appl. 14058, 1918. C. Pasques, Belg. P. 254545. P. Pipereaut, Mon. Sci. 1920, **57**, 49; abst. J. S. C. I. 1920, **39**, 401-A. Prym & Co., D. R. P. 317186, 1918; abst. J. S. C. I. 1920, **39**, 321-A. K. Quinan, U. S. P. 1348736, 1920. G. Schliebs, D. R. P. Anm. Sch-44189, 1913. H. Schneider, D. R. G. M. 498495, 1912. H. Schellhaas, Chem. Ztg. 1920, **44**, 122; abst. C. A. 1920, **14**, 2054; J. S. C. I. 1920, **39**, 265-A. Taraud & Truchot, E. P. 9461, 16866, 1911; Ital. P. 118863, 1911. H. Tobler, U. S. P. 1332581; abst. J. S. C. I. 1920, **39**, 333-A; C. A. 1920, **14**, 1190. W. Waggaman, Can. P. 171881, 1916. U. Wedge, Can. P. 162310, 1915. H. Welch, E. P. 134593, 1918; abst. C. A. 1920, **14**, 1189; U. S. P. 1328552; abst. C. A. 1920, **14**, 1190; J. S. C. I. 1920, **39**, 230-A. V. Zieren, D. R. P. 316497; abst. J. S. C. I. 1920, **39**, 356-A. Estner & Schmidt Ges., D. R. G. M. 553651. H. Pauling and Salpetersäure-Industrie-Ges., U. S. P. 1061630. P. Guye, U. S. P. 1057052. C. Bisson and A. Christie, J. Ind. Eng. Chem. 1920, **12**, 485; abst. J. S. C. I. 1920, **39**, 531-A.

1. J. S. C. I. 1910, **29**, 3; abst. C. A. 1910, **4**, 1003.
2. J. S. C. I. 1920, **39**, 64-T; abst. C. A. 1920, **14**, 1737. Concentration of sulfuric acid has been reported upon by H. Bohre, U. S. P. 1338418, Can. P. 201482; abst. C. A. 1920, **14**, 1873, 2398. C. Dähne, Gesundheitsingenieur, 1920, **43**, 145; abst. C. A. 1920, **14**, 1937. A. Düron, Aust. P. Anm. 819, 1913; D. R. P. Anm. D-27648; Belg. P. 253251, 253252. A. Gellen, Aust. P. Anm. 5616, 1911. H. Green, E. P. 27209, 1910. W. Hof, Belg. P. 260299, 1913. T. Kilroy, Can. P. 176114. Gräfläch von Landsberg-Velen u. Gemen'sche Chem. Fabrik, Berg- u. Hüttenwerke, D. R. P. 252373; D. R. P. Anm. G-32278, G-32279, 1910; Aust. P. 59310; Aust. P. Anm. 6790, 1911; Hung. P. Appl. G-67, 1910; G-3435, 1911; Ital. P. 119753, 119754, 1911. Norsk. Hydro-Elektrisk Kvaelfaktieselskab and E. Collett, Can. P. 109029; E. P. 130906; U. S. P. 1319586; abst. J. S. C. I. 1919, **38**, 945-A; 1920, **39**, 365-A; Norw. P. 23153. J. Patten, U. S. P. 1340290; C. A. 1920, **14**, 2057. H. Petersen, D. R. P. 302534, 1917. C. Stoffmehl, Belg. P. 258323, 1913. P. Vialleix and F. Perrin, Aust. P. 54965, 1912; Ital. P. 119511, 1911. A. Zanner, E. P. 19481, 1913; F. P. 462016; Ital. P. 136105, 1913; Belg. P. 250249, 1913. See also K. Reusch, Report of Sulfuric Acid Industry for 1914; Chem. Ztg. 1915, **39**, 281, 342, 398. Consult also S. Barth, D. R. G. M. 549805, 549806, 549815, 550018, 550019, 550020, 550784. F. Bräunlich, D. R. P. 70881; Hung. P. Appl. B-6356, 1913; Russ. P. 56319, 1913. G. Clark, E. P. 144869, 1920. Konsortium f. Elektrochem. Ind. Aust. P. 53534, 1912. V. Driffeld and F. Wright, U. S. P. 846288, 1907. H. Foote, J. Ind. Eng. Chem. 1919, **11**, 629; abst. Chem. Zentr. 1920, **91**, I, 815. A. Gasser, D. R. P. Anm. G-37742, 1912. P. Job and G. Urbain, Compt. rend. 1920, **170**, 843; J. S. C. I. 1920, **39**, 363-A. T. Jones, E. P. 143651; J. S. C. I. 1920, **39**, 507-A. A. Kohr, J. Ind. Eng. Chem. 1920, **12**, 580; J. S. C. I. 1920, **39**, 514-A. L. Nonnet, Belg. P. 247213, 1912. H. Reisert, U. S. P. 713800, 748308. K. Rosenstand-Wöldike, Chem. Ztg. 1920, **44**, 255; J. S. C. I. 1920, **39**, 331-A. K. Scheringa, Pharm. Weekbl. 1920, **57**, 421; J. S. C. I. 1920, **39**, 542-A. A. Smith, Amer. J. Public Health, 1920, **10**, 255; C. A. 1920, **14**, 1759. L. Winkler, Zts. ang. Chem. 1920, **33**, 59; J. S. C. I. 1920, **39**, 531-A.

CHAPTER VII.

MIXED ACIDS.

Cellulose is never nitrated by means of nitric acid alone, but always in conjunction with a water-absorbing body, sulfuric acid being universally used for this purpose. Therefore, as a preliminary to the recording of the methods of cellulose nitration which have been proposed and are employed, the physics and chemistry of mixed acids first merit consideration, and an inquiry made into the effect upon the resultant cellulose ester produced, of the variables of nitric acid, sulfuric acid, and the products of decomposition of nitric acid, in addition to the water present in commercial nitrating mixtures.

An understanding of the effect of a preponderance of one constituent over another in the esterizing bath is a preliminary to a proper conception of the factors which govern variation in the physical and chemical properties of the ester produced.

Properties of Mixtures of Nitric and Sulfuric Acids. A. Saposchnikoff¹ has examined mixtures of nitric acid with increasing amounts of sulfuric acid with regard to the partial pressure of the nitric acid; the composition of the vapor carried over by air at 25°; the vapor densities of the mixtures; and the specific conductivity. The acids used were sulfuric acid containing about 97% of the monohydrate, and the strongest nitric acid (containing, of course, oxides of nitrogen). The curves expressing the results obtained give no indication of the formation of compounds, such as the nitrosulfuric acid of Markownikoff, but point to the production of nitric anhydride to a small extent in presence of a large proportion of sulfuric acid. Experiments were also made with pure sulfuric acid monohydrate and nitric acid of sp. gr.

1. J. Russ. Phys. Chem. Soc. 1903, **35**, 305, 1098; 1904, **36**, 518; abst. Chem. Centr. 1904, **75**, I, 1322; II, 396; J. S. C. I. 1904, **23**, 865; J. C. S. 1904, **86**, ii, 251, 558; Bull. Soc. Chim. 1904, **32**, 362; 1905, **34**, 173, 787; Rep. Chim. 1904, **4**, 383; 1905, **5**, 49, 145; Jahr. Chem. 1904, **57**, 461; Meyer Jahr. Chem. 1904, **14**, 191; Zts. physik. Chem. 1904, **49**, 697; Chem. Ztg. 1904, **28**, 405.

1.478 at 15°, containing 0.4% of oxides of nitrogen. The vapor pressure of this nitric acid is only 16.64 mm., i. e., much lower than that of acid of sp. gr. 1.52. With increasing additions of sulfuric acid, the vapor pressure rises attaining a maximum in a mixture containing about 35% of sulfuric acid. Further addition of sulfuric acid causes a gradual diminution of the vapor pressure, almost in accordance with Henry's law. Analysis of the vapors showed that from mixtures containing from 100% to 30% of nitric acid, they consisted of the pure monohydrate (nitric acid); from this point onwards, the nitrogen content of the vapors increased (up to 24% of nitrogen), apparently owing to a dehydration of the nitric acid, with formation of nitric anhydride. The results show distinctly that sulfuric acid dehydrates nitric acid containing water, and makes it thereby more active for the purpose of nitration. The specific gravity, electric conductivity and vapor pressure of mixtures of nitric and sulfuric acids have been examined by him.¹

For the vapor pressure determinations, nitric acid of sp. gr. 1.5144 at 15° C., containing 98.95% of nitric acid monohydrate (HNO₃) and 0.88% of nitrogen peroxide, and sulfuric acid of sp. gr. 1.841 at 15° C., containing 98% of sulfuric acid monohydrate (H₂SO₄) were used. The results obtained are given in the following table:

| Percentage of Sulfuric Acid | Vapor Pressure in Mm. at 25° C. | Percentage of Sulfuric Acid | Vapor Pressure in Mm. at 25° C. |
|-----------------------------|---------------------------------|-----------------------------|---------------------------------|
| 0.00 | 46.20 | 49.72 | 30.30 |
| 2.77 | 41.24 | 59.90 | 25.30 |
| 9.95 | 40.80 | 69.80 | 19.38 |
| 18.79 | 40.87 | 79.77 | 12.50 |
| 29.94 | 39.10 | 89.53 | 5.00 |
| 39.76 | 34.48 | | |

For the determination of sp. gr. and electric conductivity, nitric acid of sp. gr. 1.52, containing 94.85% of nitric acid monohydrate, 2.48% of oxides of nitrogen and 2.67% of water, and

1. A. Saposchnikoff, J. Russ. Phys. Chem. Soc. 1904, **36**, 669; abst. Chem. Centr. 1904, **75**, 41, 685; J. S. C. I. 1904, **23**, 935. See J. Russ. Phys. Chem. Soc. **32**, 375; **35**, 506; Chem. Centr. 1900, **71**, II, 708; 1901, II, 1330; J. C. S. 1904, **86**, ii, 614; Bull. Soc. Chim. 1905, **34**, 1068; Rep. Chim. 1905, **5**, 186; Chem. Ztg. 1904, **28**, 574.

pure 100% sulfuric acid were used. The following results were obtained.¹

| Percentage of Sulfuric Acid | Sp. Gr. at 25°/25° C. | Electric Conductivity at 25° C. | Percentage of Sulfuric Acid | Sp. Gr. at 25°/25° C. | Electric Conductivity at 25° C. |
|-----------------------------|-----------------------|---------------------------------|-----------------------------|-----------------------|---------------------------------|
| | | Mhos. | | | Mhos. |
| 0 | 1.5100 | 479.7 ¹⁰⁻⁴ | 59.33 | 1.7898 | 714.5 ¹⁰⁻⁴ |
| 1 | 1.5131 | 422.7 ¹⁰⁻⁴ | 69.36 | 1.8213 | 761.7 ¹⁰⁻⁴ |
| 2.05 | 1.5211 | 379.0 ¹⁰⁻⁴ | 79.06 | 1.8595 | 807.9 ¹⁰⁻⁴ |
| 5.12 | 1.5397 | 433.0 ¹⁰⁻⁴ | 87.46 | 1.8807 | 905.2 ¹⁰⁻⁴ |
| 9.69 | 1.5670 | 517.5 ¹⁰⁻⁴ | 89.32 | 1.8810 | 954.7 ¹⁰⁻⁴ |
| 19.40 | 1.6192 | 619.5 ¹⁰⁻⁴ | 92.20 | 1.8734 | 1013.0 ¹⁰⁻⁴ |
| 29.31 | 1.6608 | 559.2 ¹⁰⁻⁴ | 94.75 | 1.8638 | 974.1 ¹⁰⁻⁴ |
| 38.66 | 1.7087 | 670.1 ¹⁰⁻⁴ | 97.21 | 1.8514 | 787.9 ¹⁰⁻⁴ |
| 50.36 | 1.7506 | 681.7 ¹⁰⁻⁴ | 100 | 1.8380 | 145.8 ¹⁰⁻⁴ |

In continuation of his work² Saposchnikoff has recorded the following behavior of mixtures of nitric and sulfuric acids in proportions suitable for purposes of nitration:

Vapor Pressure of Mixtures of Nitric Acid of sp. gr. 1.48 and Concentrated Sulfuric Acid. The acids used were pure 100% sulfuric acid monohydrate (H₂SO₄) and nitric acid of sp. gr. 1.467 at 15°/15° C., and containing 0.402% of higher oxides of nitrogen, so that it had the composition: nitric acid, 82.8; water, 17.2%. The results obtained are shown in the following table:

| No. | Percentage by Weight | | Composition, Per cent. by Weight | | | Vapor Pressure Mm. of Mercury | Percentage of Nitrogen in Vapors |
|-----|----------------------|---------------|----------------------------------|---------------|-------|----------------------------------|----------------------------------|
| | Nitric Acid 1.48 | Sulfuric Acid | Nitric Acid | Sulfuric Acid | Water | | |
| | 100.0 | — | 85.2 | 0.0 | 14.8 | 16.64 | 22.62 |
| 1 | 97.27 | 2.73 | 82.87 | 2.73 | 14.4 | 19.56 | 22.49 |
| 2 | 94.86 | 5.14 | 81.0 | 5.14 | 13.86 | 21.59 | 22.12 |
| 3 | 90.0 | 10.0 | 76.67 | 10.0 | 13.33 | 26.8 | 22.28 |
| 4 | 79.68 | 20.32 | 67.87 | 20.32 | 11.81 | 31.30 | 22.50 |
| 5 | 69.81 | 30.19 | 59.48 | 30.19 | 10.33 | 33.60 | 22.80 |
| 6 | 59.91 | 40.09 | 51.04 | 40.09 | 8.87 | 34.12 | 22.32 |
| 7 | 50.0 | 50.0 | 42.60 | 50.0 | 7.40 | 31.16 | 22.75 |
| 8 | 39.25 | 60.75 | 33.44 | 60.75 | 5.81 | 24.88 | 22.10 |
| 9 | 30.23 | 69.77 | 25.75 | 69.77 | 4.48 | 18.20 | 23.08 |
| 10 | 20.07 | 79.93 | 17.10 | 79.93 | 2.97 | 8.40 | 24.2 |
| 11 | 10.05 | 89.95 | 8.56 | 89.95 | 1.49 | — | 29.91 |
| 12 | 5.29 | 94.71 | 4.51 | 94.71 | 0.78 | — | — |

1. J. Russ. Phys. Chem. Soc. 1905, **37**, 374; abst. Chem. Centr. 1905, **76**, 11, 381. Zts. physik. Chem. 1905, **51**, 603, 609; **53**, 225; Chem. Centr. 1905, **76**, 11, 1152; J. S. C. I. 1905, **24**, 1031; J. C. S. 1905, **88**, ii, 583; Jahr. Chem. 1905-1908, I, 119, 120, 1795; Meyer Jahr. Chem. 1905, **15**, 94; Chem. Ztg. 1905, **29**, 350. Cf. Chem. News, 1871, **23**, 311; 1907, **96**, 106.
2. Zts. Schiess. Spreng. 1908, **3**, 201; abst. C. A. 1909, **3**, 836; Chem. Zentr. 1908, **79**, 11, 231; Meyer Jahr. Chem. 1908, **18**, 310. See C. Kullgren, Zts. Schiess. Spreng. 1908, **3**, 146; abst. C. A. 1908, **2**, 3146.

It will be seen that the vapor pressure of nitric acid of sp. gr. 1.48 (16.64 mm.), is nearly three times as small as that of concentrated nitric acid of specific gravity 1.52 (46.2 mm.); probably owing to the nitric acid forming relatively stable hydrates with the water, 1 mol. of water combining with several molecules of acid, and thereby considerably diminishing the concentration by volume of the latter. This also affords an explanation of why nitric acid alone, even when of the highest strength (sp. gr. 1.5-1.52), is not suitable for the nitration of cellulose, giving low-nitrated products; the water formed in the first stage of the nitration combines with the nitric acid to form hydrates, and in this way reduces the number of available molecules of nitric acid. The maximum vapor is attained with a mixture containing 65% of nitric acid (sp. gr. 1.48) and 35% of sulfuric acid, or almost exactly $5\text{HNO}_3 + 2\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$.

Action of Water on Mixtures of Nitric and Sulfuric Acids.

The addition of water to mixtures containing less than about 60% of sulfuric acid causes a diminution in the vapor pressure, the effect being less as the percentage of sulfuric acid is increased. With mixtures containing more than 60% of sulfuric acid, however, addition of water causes an increase of vapor pressure. This is due to the fact that with high percentages of sulfuric acid some of the nitric acid is dehydrated to nitric anhydride, which, on the addition of water, is again converted into nitric acid.

Use of Mixtures of Nitric and Sulfuric Acids in the Nitration of Cellulose.

A satisfactory acid mixture for nitration purposes must fulfill two requirements. It must contain sufficient nitric acid to give the desired reaction-velocity and degree of nitration; and its properties must not be appreciably altered by the water separated during the nitration. Mixtures which best answer the first condition have, however, the disadvantage that the volume-concentration of the nitric acid is strongly diminished by addition of water. A mixture must therefore be chosen which has a vapor pressure less than the maximum, but which will bear an addition of water without notable alteration. In the case of mixtures containing a relatively high percentage of sulfuric acid, an addition of water must be made in order to prevent dehydration of the nitric acid, with formation of nitric anhydride. The composition of acid mixtures for nitrating purposes may be

varied within wide limits, but the author considers that for the preparation of high-nitrated gun cotton, the best results will, in general, be obtained with mixtures of nitric acid of sp. gr. 1.48 with* from 65% to 75% of sulfuric acid. Probably the most suitable mixture is No. 9 in the table (see p. 1405) with the addi-

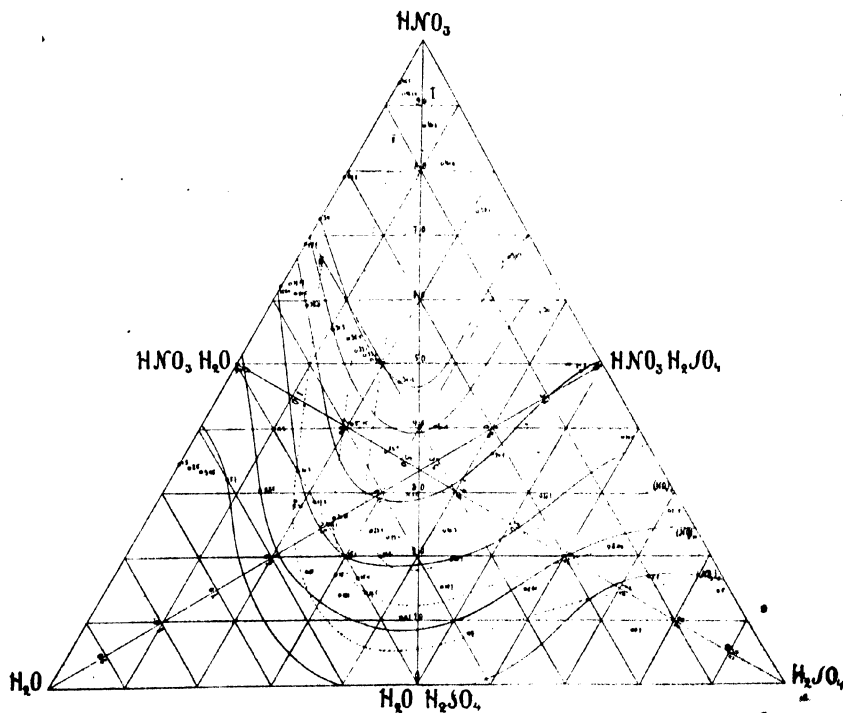


FIG. 112.—NITRATION OF CELLULOSE AS A FUNCTION OF THE MOLECULAR COMPOSITION OF MIXED ACID, AND VAPOR TENSION OF NITRIC ACID

tion of 5% of water, giving a mixture containing: nitric acid, 24.29; sulfuric acid, 65.80; and water, 9.91%.

In Figs. 112 and 113 are shown graphically the results published by Bruley, Lunge and Bebie and Saposchnikoff,¹ prepared

*1. Zts. Schiess. Spreng. 1900, **4**, 441; abst. Meyer Jahr. Chem. 1900, **19**, 333; Wag. Jahr. 1900, **55**, I, 434; C. A. 1915, **9**, 1900; J. S. C. I. 1915, **34**, 789.

by himself on triangular coordinates—the most accurate and comprehensive method of representing the composition of ternary mixtures. The numbers on the three central lines running from the corners represent the molecular percentages (not the percentages by weight), obtained by dividing the percentage by

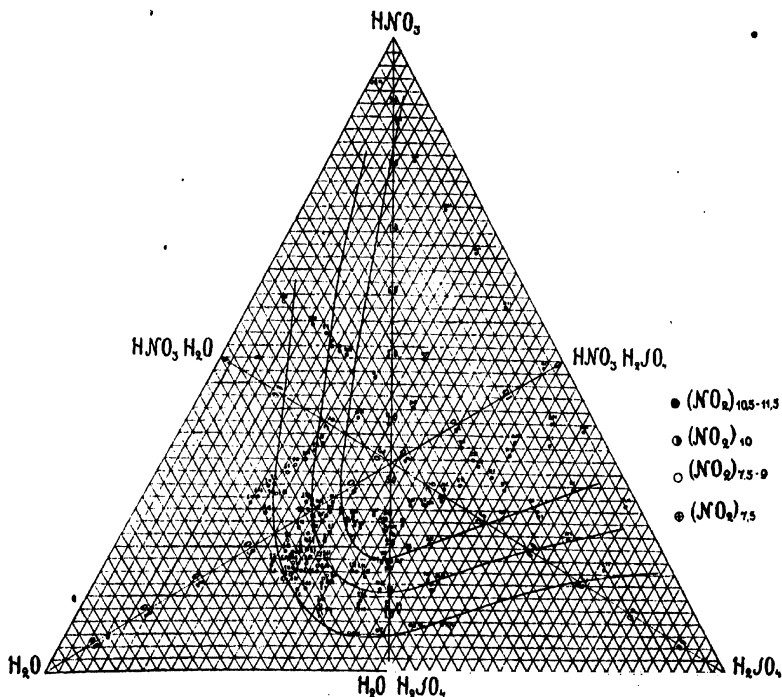


FIG. 113.—NITRATION AND SOLUBILITY OF CELLULOSE NITRATES AS A FUNCTION OF THE ACID COMPOSITION

weight of each of the three components by its molecular weight, adding the figures together, and working out the new percentages. On the same figure has also been recorded the vapor tensions, as will be observed, which have been previously discussed herein.

It will be observed that for equal percentages of nitric acid the vapor tension is at a maximum adjacent to the line joining

the points marked HNO_3 and H_2O , H_2SO_4 , which shows that when water is present in excess it combines with the nitric acid to form a less volatile compound, but on the addition of sulfuric acid this removes the water from the system, and combines with it instead. There appears no evidence of any combination of the nitric and sulfuric acids. The three curves I, II and III, show the degree of nitration of the cotton, the space inside the curve I being the region of the endeca-nitrocelluloses (about 13.5% N), that between I and II the region of the deka-nitrocelluloses (12.8% N), while between II and III are located the lower nitrates (so-called collodions) with 9 to 6 nitro-groups (12%-9% N). Beyond curve III the nitration is probably incomplete and the products formed in general are of diminished or no industrial importance.

It will be seen from an inspection of the graph that the nitration curves follow a course similar to those of the vapor pressure curves, from which it appears that the system $\text{HNO}_3\cdot\text{H}_2\text{O}$ has little action on normal or unmodified cellulose, and that the presence of sulfuric acid is necessary to liberate the nitric acid from this combination before it can act.

Saposchnikoff has demonstrated¹ that there is a close relationship between the vapor pressure of nitric acid, in mixtures of nitric acid, sulfuric acid and water, and the percentages of nitrogen in the nitrocelluloses obtained when cellulose is esterified in these mixtures. His results indicate that the highest nitrogen content is obtained when the nitric acid is in the state of monohydrate, HNO_3 , while the lowest nitration products correspond to the nitric acid hydrate, $\text{HNO}_3\cdot\text{H}_2\text{O}$. Thus, addition of 20% - 25% of water to nitric acid of sp. gr. 1.52 causes a rapid fall in the vapor pressure from 46 mm. to 9.4 mm., and it is pointed out that nitric acid of this concentration gives rise to Vieille's tetra-nitrocellulose, $\text{C}_{24}\text{H}_{36}(\text{NO}_3)_4\text{O}_{16}$. On the other hand, addition of a large excess of sulfuric acid to nitric acid of sp. gr. 1.52 causes dehydration, and consequently a lowering in the percentage of nitrogen in the resulting nitration product. Experiments carried out with a nitrating acid containing 34% of nitric acid, 61% of sulfuric acid, and 5% of water show that at temperatures vary-

¹ Zts. Schiess. Spreng. 1906, **1**, 453; abst. J. S. C. I. 1907, **26**, 34; Meyer Jahr. Chem. 1906, **16**, 324; Jahr. Chem. 1905-1908, II, 977; J. Russ. Phys. Chem. Soc. 1906, **38**, 1192; C. A. 1907, **1**, 1324; J. C. S. 1907, **92**, i, 390.

ing from 0° to 40° C., there is little variation in the products of nitration.)

According to K. Schaefer and H. Niggemann,¹ the absorption limit of 0.2-N nitric acid is displaced towards the ultraviolet even by 20% sulfuric acid, and the absorption curve being flattened at the same time, and this effect increases with increasing concentration of sulfuric acid. The sulfuric acid is considered to act as a dehydrating agent, displacing the equilibrium between the two modifications of the NO₂ group.

The thermal properties of mixtures of nitric and sulfuric acids have been examined by P. Pascal,² who represents the data in two diagrams using triangular coordinates, and in which the independent variables are water, sulfuric acid and nitric acid. The first diagram shows the boiling points under normal pressure, and the second the concentration of nitric acid in the vapor. Three dotted curves in the second diagram represent the course of distillation of three different mixtures. Over a considerable area of the first diagram, ternary mixtures with a given content of sulfuric acid show a maximum boiling point, and the concentration corresponding to this maximum is displaced towards mixtures low in nitric acid as the content of sulfuric acid increases. The temperature of the maximum boiling point, after falling slightly in the region of mixtures low in sulfuric acid, rises again to about 160° for a mixture containing 65% of sulfuric acid, and here the maximum disappears. Diminution of pressure causes a slight increase of nitric acid in the vapors, but does not alter the general character of the phenomena. The addition of sulfuric acid to concentrated nitric acid does not at first modify to any great extent either the boiling point or the concentration of the vapor, and in fact the latter is a function of the water content over almost the entire area of the diagram. There is, however, a rapid variation in boiling point in the neighborhood of mixtures usually employed to nitrate cotton, and according to

1. Zts. anorg. Chem. 1916, **98**, 77; abst. J. C. S. 1917, **112**, ii, 196; J. S. C. I. 1917, **36**, 641. C. A. 1917, **11**, 582; Meyer Jahr. Chem. 1916, **26**, 78; Wag. Jahr. 1917, **63**, I, 242. See also K. Schaefer. Zts. anorg. Chem. 1916, **97**, 285; abst. C. A. 1917, **11**, 425; Chem. Zentr. 1916, **87**, II, 980; Wag. Jahr. 1916, **62**, I, 247; 1917, **63**, II, 241.
2. Compt. rend. 1917, **165**, 589; abst. J. S. C. I. 1917, **36**, 1232; C. A. 1918, **12**, 295; J. C. S. 1917, **112**, ii, 569; Bull. Soc. Chim. 1918, **23**, 406. See also Compt. rend. 1917, **164**, 628; abst. Bull. Soc. Chim. 1918, **23**, 46.

Saposchnikoff this would explain the relative difficulty of preparing nitrocellulose intermediate between the collodion cottons and nitrocellulose of maximum nitrogen percentage. On the second diagram a curve is shown, on the right of which mixtures on distillation give vapors of continually decreasing concentration, while mixtures to the left of the curve (containing more water than the former) give on distillation vapors in which the concentration of nitric acid passes through a maximum. It can be shown that this maximum does not coincide with a maximum in the liquid under distillation, nor with a maximum in the distillate.

W. Schulte¹ has described a compound of sulfuric and nitric anhydrides and water of the formula $N_2O_5(SO_3)_4H_2O$, a water-clear, white or yellowish crystalline mass, hygroscopic and sometimes forming rectangular plates, sp. gr. 2.18, m. pt. $93^\circ-104^\circ$ and decomposing on heating with evolution of nitrous fumes; made by adding SO_3 to concentrated HNO_3 until a solution is formed from which crystals are deposited on cooling.

According to C. Meigs,² a mixture of nitrogen and sulfur dioxide is produced by burning sulfur, the nitrogen is combined with hydrogen to form ammonia, and the latter is oxidized to dilute nitric acid. The sulfur dioxide is oxidized to sulfuric anhydride, which is introduced into the dilute nitric acid to give concentrated nitric acid and dilute sulfuric acid, and the nitric and sulfuric acids are separated.

The United States Navy³ has specified that mixed acid for smokeless powder manufacture shall "consist of a mixture of nitric and sulfuric acids, which shall contain no other acids and only traces of chlorine, and no salts other than salts of iron. The acid shall contain at least 95% total acidity calculated as H_2SO_4 , HNO_3 and N_2O_4 . The H_2SO_4 shall not be more than 45.5%; the HNO_3 shall not be less than 49%; and the lower oxides of nitrogen, calculated as N_2O_4 , not more than 1%."

In practical factory scale nitration—whether cotton, glycerol or aromatic compounds—a dehydrating agent (sulfuric acid) always accompanies the nitric acid, it having been found that even the

1. U. S. P. 1047570, 1912; abst. C. A. 1913, **7**, 685; Chem. Ztg. Rep. 1913, **37**, 189; Mon. Sci. 1913, **79**, 99.

2. U. S. P. 1120960, 1914; abst. J. S. C. I. 1915, **34**, 176. C. A. 1915, **9**, 357; Mon. Sci. 1915, **82**, 19; Chem. Ztg. Rep. 1915, **39**, 270.

3. Specification 51-A-3, July 10, 1913.

most concentrated nitric acid alone, does not work satisfactorily. Probably the main function of the sulfuric acid is to combine with the water split off in the reaction and prevent its dilution of the nitric acid, but in addition, there is a large accumulation of experimental evidence in support of the statement that the sulfuric acid functions actively in the formation of small and variable amounts of sulfuric or sulfonic esters, whose presence, even in small amounts, is intimately associated with the stability of the final product, especially where this product is the highly nitrated celluloses.

The nitric and sulfuric acids used in such immense quantities in the period 1914-1918, in general, were commercial products of a high degree of purity. The sulfuric acid should be as free from lead as possible, and the nitric acid contain no hydrochloric acid. It is also highly important that neither acid should contain solid impurities which might possibly adhere to the nitrated cellulose, or which might interfere with the subsequent recovery of the waste acid.¹

Fortification and Acid Recovery. After nitration, the spent acid, richer in water and sulfuric acid and weaker in nitric acid, is usually run by gravity into a sump or tank, where by means of compressed air it is blown into storage tanks and there allowed to cool before being purified or fortified. Restoration of used acid is usually comprized in the three following steps:

1. Elimination of impurities (fibers of cotton and nitrated cotton) in suspension by purely physical means.
2. Removal of nitrogen oxides.
3. Increasing the percentage of nitric and sulfuric acid by the addition of new acid so the composition is brought to a definite percentage constant.
4. Mixing the used and unused acid to form a new homogeneous nitrating mixture.

In practice 3 and 4 are practically one series of operations.

Clarifying Spent Acid. In addition to varying proportions of oxides of nitrogen in solution, spent acid contains small amounts

1. For action of HNO_3 on cellulose, see H. de Mosenthal, J. S. C. I. 1904, **23**, 292; 1897, **26**, 443; J. C. S. 1911, **100**, i, 711; Jahr. Chem. 1904, **57**, 1166. J. S. C. I. 1907, **26**, 443; C. A. 1907, **1**, 1770; Zts. ang. Chem. 1907, **20**, 1970; Jahr. Chem. 1905-1908, 975; J. Soc. Dyers Col. 1907, **23**, 214; C. N. 1907, **95**, 189. J. S. C. I. 1911, **30**, 782; C. A. 1911, **5**, 3153; J. C. S. 1911, **100**, i, 711; Chem. Centr. 1904, **75**, I, 1625, 1646; 1907, **78**, II, 687, 2039.

of cotton fiber and of nitrated cotton in suspension which it is desirable to remove before reuse. These are mechanically eliminated by filtration, through acid washed sand or shredded asbestos filters, or less often, a filter composed of highly nitrated cellulose—usually nitrocotton.

In 1882 F. Pool¹ obtained patent protection for an improved process for removing flocculent matter from spent acids used in the treatment of soluble fiber, by which he proposed to eliminate from the spent acid contaminated with "flock" of cellulose by the addition of barium sulfate in powdered form, agitating the spent acid with the barium sulfate and allowing the whole to stand until precipitation has occurred. The insoluble barium sulfate mechanically carries to the bottom the fibers in suspension, thus leaving a substantially clear solution. He found that when a tank four feet in depth, containing some 680 gallons of nitric and sulfuric acids is treated with 30 pounds of finely powdered barium sulfate, precipitation will be satisfactorily effected in from 36 to 70 hours. Of course the amount of settling agent required varies according to the consistence and the amount of insoluble matter in suspension in the spent acid.

E. Allary² has proposed to clarify the waste acid in the manufacture of nitrocellulose by filtration through finely powdered quartz either as powdered quartz or sharp sand, subsequently obtaining the nitric acid therefrom by distillation. He has found that the waste acid can be used to produce nitric acid of 48.4° Bé., preheating it with sodium nitrate in the usual manner. The following material of J. Porter,³ claimed as especially useful for nitrating acid, is formed of 75% to 85% quartz sand and 25% to 15% of powdered glass, fused together at a temperature of 1040° to 1700°, depending on the kind of glass used. The so-called "carbon stone" of S. Bornett⁴ is obtained by grinding coke of low

1. U. S. P. 251938, 1882. J. Hyatt and F. Pool, U. S. P. 274335, 1883. M. Lefferts, E. P. 24, 1882; abst. J. S. C. I. 1882, **1**, 32.

2. Bull. Soc. Chim. 1887, (2), **47**, 102; abst. Wag. Jahr. 1887, **33**, 570; Vide, J. A. C. S. 1886, **8**, 171; 1887, **9**, 38; J. C. S. 1887, **52**, 770; Chem. Ind. 1887, **10**, 190; Paint, Oil & Drug. Rept. 1887, **13**, 9, 13; Proc. U. S. Nav. Inst. 1887, **13**, 419.

3. U. S. P. 1117601, 1914; abst. C. A. 1915, **9**, 4; J. S. C. I. 1915, **34**, 16. See J. Porter, U. S. P. 1118441, 1914; E. P. 22080, 1914; abst. J. S. C. I. 1915, **34**, 69, 1197.

4. D. R. P. 241710, 1909; abst. C. A. 1912, **6**, 2151; Chem. Zentr. 1912, **83**, I, 170; Chem. Ztg. Rep. 1912, **36**, 27; Wag. Jahr. 1911, **57**, I, 651; Zts. ang. Chem. 1912, **25**, 128.

ash content, mixing it with about 20% tar and stamping in forms, and then burning with the exclusion of air. This material, it is claimed, can also be used for the filtration of highly concentrated boiling hot solutions of caustic potash or caustic soda without being appreciably attacked. The C. Brockbank apparatus for filtering corrosive liquids¹ and shown in Fig. 114, comprizes a filter plate formed of carborundum without any binder and the supports 5 and suction bell 3 are formed of silica or an acid-resisting silicon alloy.

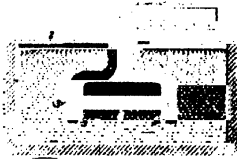


FIG. 114.—THE BROCKBANK APPARATUS FOR FILTERING CORROSIVE LIQUIDS

Filtration through a fine mesh platinum sieve has been recommended, but the cost of such a sieve has precluded its general use for this purpose. In the Thomson displacement method of nitration there is but little cotton or other flocculent matter in suspension in the used acids, due to the fact that they are so accurately removed from the nitrating cellulose that the latter acts as a filter to retain all the fine, solid particles.

In the two methods of acid mixing, i. e., agitation and by air, mechanical agitation by means of a stirring arrangement provided with paddles is used when a horizontal mixing tank is employed, and in this instance preferably mixed while the acid is on the scales, when other acid can be added thereto, and the mixing continued to the proper composition. With a vertical tank—where the length is several times the diameter—agitation by compressed air is preferable. In this method there is a maximum and usual loss of 0.1% nitric acid from the fumes blown out in the process of blowing in agitating the acid—which on large scale factory operations is a point not to be lost sight of.

Recovery and Fortification of Spent Acid. Frequently acid from the manufacture of nitrocellulose is usually revived by the

1. U. S. P. 1152875, 1915; abst. C. A. 1915, **9**, 2728. In respect to the lower oxides of nitrogen, J. Pitman (J. S. C. I. 1900, **19**, 645) has observed that in purchasing mixed acids for nitration purposes, these oxides are usually limited to a maximum of 0.05% calculated as N_2O_5 . After rebuilding the used acid a number of times, the lower oxides will increase to 0.2%–0.3%. According to Pitman, if these lower oxides are neglected in calculation or considered as nitric acid, the gun cotton formed therefrom will be substantially the same.

addition of fuming sulfuric acid (oleum) and concentrated nitric acid, for by the use of 30% oleum it has been found possible to indefinitely fortify waste acid, so that at the present time it is usually unnecessary to discard any of the spent acid from the nitrating process. Before the advent of oleum as a commercial commodity, it was found impossible to indefinitely strengthen by the addition of sulfuric and nitric acids each time, the quantity of spent acid remaining from the nitrating process. It therefore became necessary after each nitration to discard a portion of the nitrating acid. This, especially, was found true in the displacement process where the amount of waste acid is considerably more than in the centrifugal method, for the recovery of the waste acid is much more complete as some of it becomes diluted with water used for the displacement. By the employment of oleum of 30% to 60% and nitric of 95% and higher, it has been found that indefinitely rejuvenation of spent acid is possible, so that its use becomes a continuous cycle. In those factories having arrangements for recovering nitric acid, it has been found more economical in general to use oleum of 20% to 30% strength. When the nitration process has been properly carried out the refortified acids are but little less efficient than new acid, at least in the manufacture of the higher nitrogen compounds of cellulose. The organic impurities formed in small amounts in the nitration process either are washed away in the purification of the nitrated product, or are completely oxidized by the nitrating mixture if they have passed into solution. The quantity of organic impurities remaining in the acids, therefore, is comparatively small.

W. Will has found nitrosugars in waste nitrating acids, while others have reported the presence of appreciable quantities of oxalic acid.

In the process of W. Poetsch¹ for the treatment of waste acid after nitration, the acid is heated to 105° whereby the nitro-compounds contained in solution are supposed to be destroyed, while part of the nitric acid is reduced. By means of the heat evolved, the nitric acid is partially volatilized, but may be re-

1. D. R. P. 29664; abst. *Wag. Jahr.* 1884, **30**, 371; *Bied. Tech. Chem. Jahr.* 1886, **7**, 150; *Chem. Ind.* 1884, **7**, 355; 1885, **8**, 114; *Industrieblätter*, 1885, 16; *Chem. Tech. Rep.* 1884, II, 160; *Ding. Poly. J.* 1885, **255**, 216; *J. S. C. I.* 1885, **4**, 243; *Ber.* 1884, **17**, R, 596, 625; *Jahr. Chem.* 1884, **37**, 1752. See M. Schall, *Zts. Schiess-Spreng.* 1917, **12**, 57; *C. A.* 1918, **12**, 631.

covered by an arrangement consisting in the main, of a stoneware vessel with a sieve bottom and filled with pieces of clay. The denitrated sulfuric acid flows off at the bottom while the nitrous oxides are oxidized with air and recovered in large Woulfe bottles.

C. Claessen,¹ after nitration and centrifugalizing of the nitrated material, injects sulfuric acid in the running centrifuge, whereby the nitric acid retained in the nitrating mass is thus replaced by the less expensive sulfuric acid, the latter being recovered by injecting water. In this manner a larger proportion of spent nitrating acid is said to be recoverable.

The method for restoring the strength of nitrating baths in the manufacture of guncotton, as devised by G. Mowbray² and shown in Fig. 115 was at one time used on a considerable scale

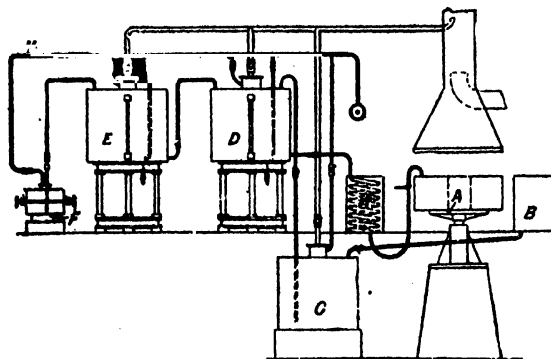


FIG. 115.—MOWBRAY APPARATUS FOR RESTORING NITRATING BATHS

in the United States. The nitrating tanks are eight in number, arranged upon a turn-table A, the tanks being filled with a standard mixture and are then charged with cellulose, which after

1. D. R. P. 200292, 1906; abst. Wag. Jahr. 1908, **54**, I, 432; Zts. ang. Chem. 1908, **21**, 1854; Chem. Zentr. 1908, **79**, II, 559; Chem. Ztg. Rep. 1908, **32**, 445; Chem. Ind. 1908, **31**, 505; Mon. Sci. 1911, **74**, 93; J. S. C. I. 1908, **27**, 961; Zts. Schiess. Spreng. 1908, **3**, 335.

2. U. S. P. 350497, 1886; abst. J. A. C. S. 1886, **8**, 239. E. P. 13011, 1886; abst. J. Soc. Dyers Col. 1886, **2**, 191; J. S. C. I. 1886, **5**, 688. In Zts. Schiess. Spreng. 1914, **9**, 317, 329. A. Oelker has tabulated the patents covering the period 1886-1914 relating to nitric acid manufacture, including 77 patent specifications.

treatment in the required time the mixture is placed in the centrifugal separator *B* to remove the spent acid and store it in the tank *C*. The deficiency in each nitrating tank caused by the removal of the wet nitrocellulose is then made up from the tank *D* which contains a mixture of acids of higher strength than the standard mixture, so that upon mixing with the weakened acids in the tank the whole will be up to the strength of the standard mixture. The tank *D* is charged from the spent acid tank *C* and the concentrated acid tank *E*. *F* is the weighing machine upon which the drums of acids are placed, the acid being then discharged into tank *E* by forcing compressed air down the pipe *H* into the drum. Compressed air is also used for charging tank *D* from the tanks *C* and *E*. *K* is the coil for controlling the temperature of the mixture from the tank *D* to the nitrating tanks.

F. du Pont¹ has devised a centrifugal machine for continually separating the acid from guncotton, thereby effecting the saving of labor and insuring a more constant condition of operation in the separation, and which at the same time provides means for continuously feeding in a proper manner the material through the centrifugal machine and also provides certain simple mechanisms by which the machine is moved relatively slowly for driving the parts of the centrifugal machine at a high speed, yet with the necessary relative difference of speed between the gears. The principle is shown in Figs. 116 and 117, in which it will be seen that the guncotton and acid are continuously fed through the hopper *21* and tube *8* through the spaces between the arms of the spider *4* into the interior of the rapidly rotating perforated cylinder *2*, the material being continuously fed into the perforated cylinder *2*. This is rapidly rotated upon the horizontal axis and subjected to centrifugal action, the acid passing through the perforated wall of the cylinder and escaping into the casing *1* and thence by the off-take *15*, the guncotton, of course, remaining in the perforated cylinder. As the guncotton thus becomes freed from acid it is fed through the horizontal rotating cylinder *2* and escapes at the left-hand end, past the arms of the spider *3* into the chamber *17* and thence by way of the off-take *17*. The feed of the material through the rotating horizontal cylinder is controlled

1. U. S. P. 1024624, 1912. A. Charles, E. P. Appl. 9088, 1916. R. Chatfield, E. P. 19512, 1891; abst. Mon. Sci. 1893, **42**, 142.

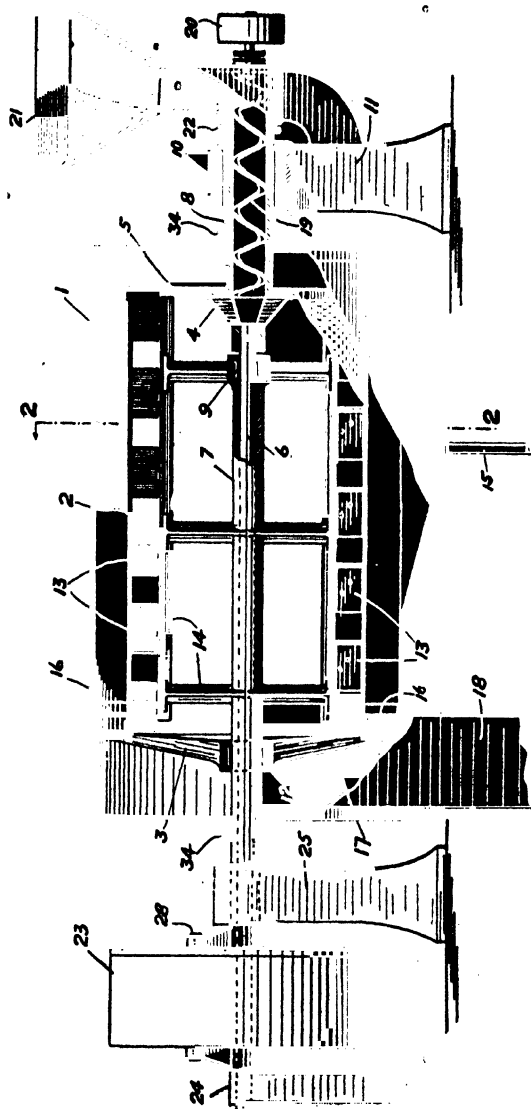


FIG. 116.—DU PONT SYSTEM FOR REMOVAL OF ACIDS FROM NITROCELLULOSE

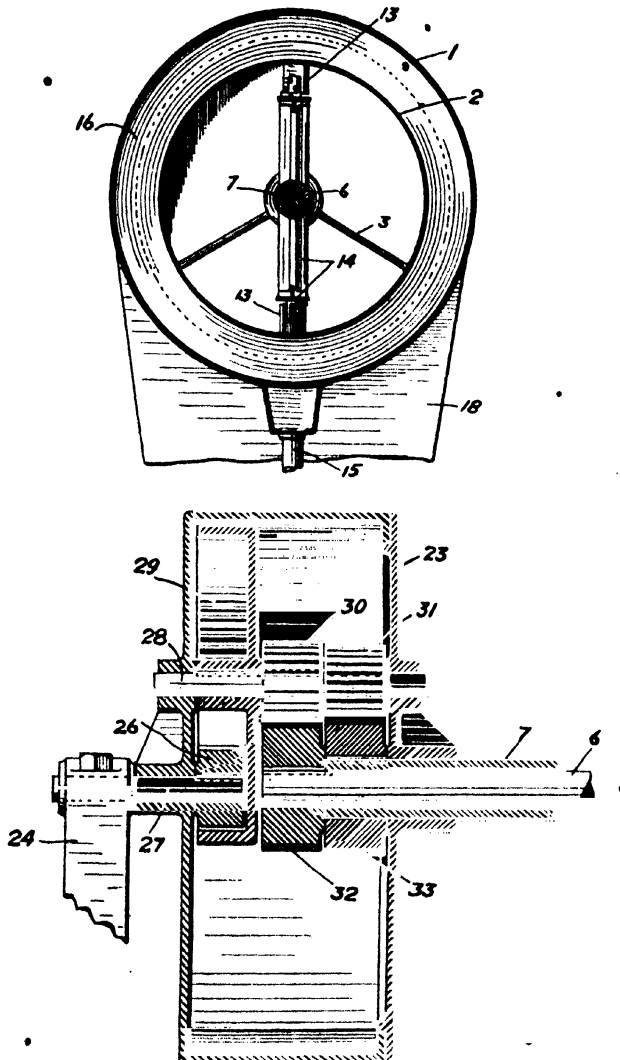


FIG. 117.—DU PONT SYSTEM FOR REMOVAL OF ACIDS FROM NITROCELLULOSE

and governed by the speed of the slanting blades or feeders 13, which rapidly revolve, yet more slowly than the perforated cylinder, and this difference in speed is important because it admits of a desirable yet continuous feed for giving rise to a continuous stream of acids, and likewise a continuous stream of nitrating cotton. To prevent leakage of both liquid and air so that air is excluded from the casing, stuffing boxes or glands, 34, are applied between the ends of the housing or casing and the in-take tube 8 to the sleeve 7. According to the claims of the patentee, the nitrocellulose subjected to the process which is outlined, is maintained out of contact with air so that the former, as well as the apparatus itself, are prevented from undergoing those chemical changes due to moisture in the atmosphere. The point claimed is that better and more uniform results are obtained by the removal of acids from the nitrocellulose when the atmospheric air is excluded because the moisture may, and is quite apt to induce certain undesirable chemical changes in the nitrated product.

A process for renewing waste acids from nitration as patented by the Salpetersäure Industrie Gesellschaft¹ depends upon the concentration of nitric acid by electrolysis. The patentees claim this method of concentrating is applicable for any degree of acid, even the pure monohydrate, and is characterized by the conduction of the nitrogen oxides formed at the coil into the liquid surrounding the anode, where they dissolve and are oxidized by the oxygen at the anode into nitric acid. It is advantageous in this method to cool the nitrogen oxides before passing them into the nitric acid surrounding the anode so that the NO_2 is liquefied, and drops in this form into the HNO_3 . NO_2 mixes much more readily with the anode liquor when liquefied where the gas is difficultly soluble, and in order to bring it into solution, working under pressure would be necessary. The reaction should be so conducted that the nitration of the acid does not become too low; also that the current strength does not rise too high so that nitrogen is produced. The working of the process must be so

1. D. R. P. 180052, 1905; abst. Chem. Zentr. 1907, **78**, I, 1083; Chem. Ztg. Rep. 1907, **31**, 86; Zts. ang. Chem. 1907, **21**, 1323; Wag. Jahr. 1903, **51**, 446; Jahr. Chem. 1905-08, I, 1794; Chem. Weekblad, 1907, 1083. D. R. P. 180587, 1903, addition to D. R. P. 180052, 1905; abst. Zts. ang. Chem. 1907, **20**, 1196; Chem. Zentr. 1907, **78**, II, 115; Chem. Ind. 1907, **30**, 90; Wag. Jahr. 1907, **53**, I, 419; C. A. 1907, **1**, 2436.

adjusted that only NO and NO₂ are formed, thereby giving a method in which there is considerable latitude as regards concentration of the acid employed and the current strength. The acid to be concentrated is profitably previously saturated with nitrogen oxides so that the oxygen formed at the anode will find some oxidizable material at the commencement of the process, and thereby will not escape as such.

The method of fortifying by the addition of a crystalline nitrate (usually sodium or potassium nitrate) and depending on the sulfuric acid in the nitrating mixture for the liberation of nitric acid *in statu nascendi* has been discarded on account of interference by the large amount of potassium or sodium sulfates formed by the interaction of the sulfuric acid on the nitrate.¹ The use of a nitrate soluble in water, the corresponding sulfate of which is insoluble (calcium, strontium, barium) has proven unsatisfactory in that it introduces another operation, that of filtering off the precipitated insoluble sulfate, and additional expense is introduced into the process from the excess amount of sulfuric acid required to unite with the base.² The process of S. Mackie and C. Fauré is similar,³ except they employ barium carbonate and subsequently eliminate the CO₂ formed by the interaction.

A. Hollings, G. Jarvis and G. Bell⁴ have described an apparatus especially applicable for treating and recovering the used acids from the manufacture of nitrocotton where more uniform distribution of air in liquids is required. A chamber which is inserted in the liquor to be treated is provided externally with one or more series of concentric rings or division pieces. This chamber is filled with air or gas, delivered through suitable perforations in the bottom or sides, or between the rings. In the R. Sohlman and W. Wilson process of concentration designed

1. F. Pool, U. S. P. 306519, 1884; 336822, 1886; 343850, 1886; abst. Wag. Jahr. 1886, **32**, 319; J. A. C. S. 1886, **8**, 68, 171. See also H. Maxim, U. S. P. 479988, 1892; abst. J. A. C. S. 1892, **14**, 295. A. Nobel, E. P. 1813, 1864; abst. Mon. Sci. 1874, **16**, 1031; 1905, **65**, 84.

2. J. Hyatt and F. Pool, U. S. P. 274335, 1883. F. Pool, 343850, 1886. The most elaborate and expensive system of nitrating acid fortification is probably that of J. Hyatt, F. Pool, J. Everding, J. Stevens and W. Wood (U. S. P. 299388, 1884), designed for handling large quantities. It has been estimated that its equipment and installation would cost at least one hundred thousand dollars.

3. E. P. 3612, 1874.

4. E. P. 12286, 1901; abst. J. S. C. I. 1902, **21**, 904.

especially for the treatment of waste nitrating acids,¹ the mixture of acids to be treated flows continuously through a vertical conduit or column of acid-proof material filled with silica and heated externally, a current of hot air or other gas being led in the opposite direction through the conduit or column. The liquid is fed into the top of the closed chamber, subdividing it into even streams during its descent through the chamber by means of acid-proof contact surfaces, these streams coming in contact with the continuous current of a hot vaporizing gas which is cooled during its ascent among the subdivided streams and also exteriorly heating the chamber by continuous currents of hot gases.

W. Dreger² has proposed to minimize the loss of nitrating acid in the water used for drowning the nitrating charge by washing each freshly nitrating charge with the wash water from the previous charge. Six nitrators are arranged in about the center and so connected that the spent acid may be drained from each as desired, then water added and transferred in succession from one to the next by means of compressed air. Each nitrating charge is thus washed six times with the acidified water from the charge ahead of it, the water not being withdrawn and replaced by fresh water until it no longer increases appreciably in acidity. The nitrated cotton, after six washings in waters of various acidities is washed once more with fresh water, withdrawn, and then given further hot washings in the usual method. Apparently the main idea of the process is the economy on acid waste without, however, sufficient regard to the uniform subsequent stability of the nitrated product.

It was R. Schüpphaus who first patented the use of sulfuric anhydride for the replenishing of spent nitrating acids.³

In the case of the process of H. de Chardonnet⁴ for the purification of nitric acids used in the esterification of cellulose, the waste acid mixture is heated up to 170°, at which temperature the nitric acid readily distills off, the nitric acid thus being separated from the sulfuric and thereby freed from solid impurities

1. U. S. P. 1009196, 1911; abst. C. A. 1912, **6**, 277; Mon. Sci. 1912, **77**, 130.

2. Zts. Schiess. Spreng. 1913, **8**, 325; abst. C. A. 1913, **7**, 3840.

3. U. S. P. 526752, 1894; abst. Mon. Sci. 1895, **46**, 73. E. P. 18683, 1894; abst. Chem. Ztg. 1896, **20**, 204.

4. D. R. P. 56655, 1890; abst. Mon. Sci. 1894, **44**, 29; 1905, **65**, 321; Ber. 1891, **24**, 1004; Wag. Jahr. 1891, **37**, 1113; Zts. ang. Chem. 1891, **4**, 466.

by the process of distillation, and mixed with further amounts of nitric and sulfuric acids for nitrating purposes.

The use of waste spent nitrating acid for the manufacture of acid phosphate, as advocated by V. Tribouillet and L. de Besaucele¹ has, so far as aware, never been operated commercially.

Kynoch & Company, Ltd., and A. Cocking² purify and concentrate mixtures of sulfuric and nitric acids by placing the acids to be purified and concentrated in a cast iron or other suitable still capable of withstanding atmospheric pressure, and exhausting by means of a pump to produce a partial vacuum within. During the exhausting process heat is applied to the acid from outside and under the combined influence of reduction of pressure and the application of heat, nitrous fumes of the acid are disengaged and carried away to be suitably condensed or absorbed. When the nitrous or other fumes have been driven off the heating and evacuating is continued and in time the sulfuric acid loses its water and becomes more concentrated.

C. Kaesemacher utilizes the waste acids from nitrating processes by combining the separation and concentration by the old process by running them down a tower intercepted with acid-proof materials where they meet an ascending stream of hot air.³ The process as patented in the U. S. by F. Jensen is now antiquated.⁴

E. Hartmann⁵ concentrates waste acid from nitrating processes up to 61° Bé (sp. gr. 1.732) in six lead pans, after which the acid at a temperature of 145° to 150° passes through a small preliminary cast iron pan which is provided with a lead hood and a chimney for removing vapors which contain but little acid. In this manner a concentration represented by a sp. gr. 1.785 to 1.796 is obtained, at which point the acid is allowed to run into cast iron pans with cast iron covers, one placed above the other, wherein the sulfuric acid is then concentrated to 97% to 98%.

A. Pohl and the Deutsche Ton- und Steinzeugwerke⁶ denitrate in columns made of quartz-glass about 10" wide and 9' 6"

1. E. P. 5057, 1878; abst. J. S. C. I. 1895, **14**, 14, 180.

2. E. P. 28891, 1896. E. P. 22717, 1896; abst. Arms and Expl. 1897, **6**, 32.

3. E. P. 2382, 1908; abst. J. S. C. I. 1908, **27**, 1019. E. P. 383783; abst. Chem. Ztg. Rep. 1908, **32**, 389.

4. U. S. P. 284742, 1883. Cf. P. Castellanos, U. S. P. 164200.

5. Chem. Ztg. 1899, **23**, 147; abst. Chem. Centr. 1899, **70**, I, 1300.

6. Zts. ang. Chem. 1912, **25**, 1853; abst. C. A. 1912, **6**, 3170.

high, in which, when heated by steam at 200°, 8 tons of waste acid containing up to 3% nitric acid may be successfully treated in 24 hours. Each column consists of iron pipes of 2' 6" diam., fitted with quartz rings, resting on a perforated plate, the superheated steam being introduced in the center of the bottom pipe by means of a tube of such shape that the steam blows straight upwards. The nitric acid vapors issue from the top of the tower into a very cool receptacle consisting of five quartz glass tourelles of 2.65 cubic feet capacity, each with vertical tubes; the vapors not condensed there pass on to the wash tower filled with pieces of quartz.

The nitric acid recovery processes of J. Leitch¹ and R. Craig, et al.,² are more applicable to the waste acid from the nitration of toluene.

For the recovery of nitric acid in nitrating mixtures, S. Stollenwald,³ V. Vender⁴ and F. Nathan and J. and W. Thomson,⁵ have obtained patent protection.

The removal of nitrogen oxides is accomplished in several ways, the most important method being to blow compressed air through the mass, thus driving the gases out of solution, which are then led through condensing towers of brick or volcanic stone and into a weak alkali solution, forming nitrates and nitrites useful as fertilizers. Another plan proposed is to eliminate the oxide by gentle heating of the mixed acid but the disadvantage of this suggestion is that nitric acid also is volatilized.

Aspirating cold air through spent acid is tedious and not always successful and calls for previous drying of the aspirated air. Physical absorption with pumice stone has been disappointing. A system of aeration in which the spent acid in a thin stream is allowed to meet a heavy blast of air has apparently not fulfilled the claims of the inventor, due to the inevitable weakening of the spent acid, if the volume of air is sufficiently increased to substantially eliminate all the oxides. The amount of nitrogen oxides present in the majority of instances is less than 1%, and

1. E. P. 15455, 1915; abst. J. S. C. I. 1916, **35**, 869. C. A. 1917, **11**, 1304.

2. E. P. 23181, 1914; abst. J. S. C. I. 1915, **34**, 985.

3. Aust. P. 42408, 1910.

4. Aust. P. 43749, 1910.

5. Belg. P. 218933, 1909. See also E. P. 10171, 1909. F. P. 406806; abst. J. S. C. I. 1910, **29**, 564; Chem. Ztg. Rep. 1910, **34**, 151.

in many nitrating houses this amount is neglected and is not eliminated. The degree to which the nitrating acid has been weakened by the process of nitration will depend upon:

(a) The amount of nitrogen introduced into the cellulose. The higher the cellulose nitrate the greater the nitric acid extracted per unit weight of cellulose esterified.

(b) The method of nitration used. There being less loss of nitric acid and nitrogen oxides in the air with the displacement method than with the hand, pot or centrifugal nitration processes.

(c) The temperature of nitration. The higher the temperature the greater the loss of nitric acid from evaporation.

(d) The extent of "fuming" in the individual nitrations. The greater the "fuming" (that is, liberation of nitric oxides) the weaker will the spent acid become in nitrogen.

It must be remembered that in the nitration of benzene, toluene and other aromatic compounds required in the manufacture of dyestuffs where the waste acids contain but little nitric acid, generally only about 1%, and with nitrobenzene usually less than 0.3%. The case is entirely different, however, with the waste acid from the manufacture of explosives, where the nitric acid content is much higher than those from the manufacture of nitrobenzene. A typical nitroglycerol waste acid will have the composition of about HNO_3 10%, H_2SO_4 70%, H_2O 20%, whereas the acid from guncotton manufacture will contain nitric acid 11% to 14%, sulfuric acid 80% to 84%, while the balance is water.

To guard against accidents caused by leaking valves or corroding pipes, it is advisable to leave the spent acid in storage tanks until shortly before use, these tanks being located by gravity so that in the event of leaks in valves or pipes, no acid will run out. The fortified nitrating acid which consists of (a) the maximum in percentage of used acid which when combined with (b) sulfuric acid either 98% or sulfuric acid 98% containing varying amounts of oleum, and (c) a mixture of nitric acid 50% to 60%, of sulfuric acid 45% to 35% or less often (in the United States) 98%.¹ The composition of the spent and strength of the

1. R. Schüpphaus (U. S. P. 526752, 1894; abst. Mon. Sci. 1895, **46**, 73. *U. S. P.* 18683, 1894; abst. J. S. C. I. 1894, **13**, 1220; Chem. Ztg. 1896, **20**, 204) was the first to patent the strengthening of nitrating acids by the use of sulfuric anhydride. It is a question not fully ascertained whether the

fortifying acids having been obtained analytically they are mixed in certain proportions⁹ to produce the desired mixture.

In the C. Kaesmächer process of separating nitric from sulfuric acids,¹ and concentrating the latter, the acid liquid is finely divided by means of refractory materials contained in a suitable tower, and subjecting the finely divided liquid to the action of a current of hot air for the purpose of simultaneously concentrating the sulfuric acid and separating it from the nitric acid without dilution.

As advised by F. Zeisberg,² acid mixtures containing 64% or more of H_2SO_4 and from 3%-25% HNO_3 , such as spent acids from nitrating cellulose, are treated with a current of hot gases and steam, and the nitric vapors carried away and condensed. He has described and illustrated a concentrating tower for carrying out the process.

The essence of the invention of J. Brooke³ consists in taking waste acids such as are produced in making picric acid, and concentrating them in earthenware, enameled or other acid-proof vessels provided with coils or jackets through which pressure or superheated steam is circulated. A battery of vessels, each fed from a pipe and discharging into a trough may be used, the vapors being led to a fume pipe. Alternately the vessels may be arranged so that the acid flows through them in series.

The W. Furness filter press plate, for filtering waste acids,⁴ comprises a frame provided with tightening bolts extending through the top and bottom bars of the frame enclosing filter panels of earthenware or other acid-resisting material. The panels have vertically grooved surfaces, the lower ends of the grooves communicating with discharge channels in the frames. Those parts of the frame which are exposed to the action of the acids are protected by a lead or other suitable covering.

In the process for producing mixtures of sulfuric and nitric use of the anhydride is prejudicial in any way to the nitrated cotton. For the recovery of nitric acid in the quartation of silver alloys, see D. Fitzgerald, E. P. 6371, 1884; abst. J. S. C. I. 1885, **4**, 225; Wag. Jahr. 1886, **32**, 203.

1. E. P. 2382, 1908; abst. C. A. 1909, **3**, 1330; J. S. C. I. 1908, **27**, 1019.
2. U. S. P. 1292048, 1919; abst. C. A. 1919, **13**, 998; Mon. Sci. 1919, **36**, 48.
3. E. P. 120051, 1917; abst. C. A. 1919, **13**, 640; J. S. C. I. 1919, **38**, 92-A.
4. E. P. 124974; abst. J. S. C. I. 1919, **38**, 313-A.

acids as perfected by J. Nield,¹ gaseous sulfuric anhydride is passed upwards through a scrubber into the upper part of which a mixture of sulfuric acid and weak nitric acid is sprayed. From the mixed acid discharged at the lower end of the scrubber, a portion is withdrawn as final product. The remainder is mixed with a further quantity of weak nitric acid, any nitric acid vapor evolved is condensed and returned to the mixed acid, and the latter is cooled and again sprayed into the upper end of the scrubber.

In the method of F. du Pont² the retort in which the nitric acid is generated is connected to an absorber containing sulfuric acid, by circulating conduits, one of which conveys the nitric acid vapor to the absorber, while, by the aid of a blower, the other conduit returns the unabsorbed gases. The absorber is preferably fitted with an agitator.

O. Guttman³ maintains that a perfect mixture of nitric and sulfuric acids may be made by simply running the sulfuric into the nitric. However, it is almost the universal practice to agitate the mixture either by compressed air or by stirring. With the former the elimination of nitrogen oxide fumes is of additional advantage. The compressed air⁴ may be first cooled and dried by refrigeration, as suggested by E. Hasketh and F. Willcox.

In order to facilitate the condensation of the acid fumes and their admixture with the liquid, and at the same time safeguard the destruction of the mixing apparatus by the solvent action of the fumes, F. Du Pont⁵ has designed a plurality of condensing chambers arranged in series (see Fig. 118) and connected together at the top and bottom, the first chamber being also connected with a retort or other apparatus for generating the acid fumes to be condensed. A cooling tank is also provided and connected to

1. U. S. P. 884035, 1908; abst. J. S. C. I. 1908, **27**, 447; Mon. Sci. 1909, **71**, 28; Chem. Ztg. Rep. 1909, **32**, 283; C. A. 1908, **2**, 2432; Zts. Schiess. Spreng. 1909, **4**, 154.

2. U. S. P. 743922, 1903; abst. J. S. C. I. 1903, **22**, 1292; Chem. Zts. 1904, **3**, 244, 400.

3. Proc. Inst. Civil Eng. 1901, **143**, 1; abst. J. S. C. I. 1901, **20**, 836.

4. E. P. 1416, 1905; abst. J. S. C. I. 1905, **24**, 1084; Zts. Schiess. Spreng. 1906, **1**, 17.

5. U. S. P. 736625, 1903; abst. Mon. Sci. 1903, **59**, 182; J. A. C. S. 1904, **25R**, 140. For description of air compressors for pumping acids, see Anon., C. A. 1909, **3**, 1575. The T. Briggs acid-distributing apparatus, is described in U. S. P. 1032657, 1912; abst. C. A. 1912, **6**, 2676.

the condensing vessels, being provided with means for cooling the liquid within it, and also for inducing circulation.

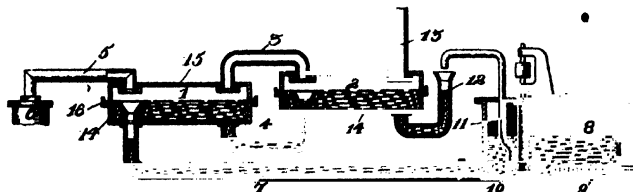


FIG. 118.—THE DU PONT APPARATUS FOR CONDENSING AND MIXING ACIDS

The invention of P. Castellaos¹ relates to the manufacture of nitro-sulfuric acid, especially designed for the manufacture of nitroglycerol, considerable economy of both time and material being claimed. The acid mixture is obtained at the time of nitric acid manufacture by the use of sulfuric acid vapors as a condensing agent, the niter and sulfuric acid being introduced into a retort, and heated. The retort communicates with a series of vessels containing instead of water or dilute nitric acid, sulfuric acid which condensed the nitric acid as it is distilled over, and forms a compound therewith. This compound is then used for nitrating purposes.

Irrespective of the particular method of acid mixing employed, it is customary where possible to arrange the tanks at such a height that their contents will flow by gravity into the weighing tank scales, and thence into the nitrating house.

The spent acid is pumped into one of the storage tanks, the other two containing the sulfuric acid and the nitric acids respectively. Of the various mixing scales in use, in the United States, those of Fairbanks Co. of New York, shown in Figs. 119 and 120, has proven satisfactory, both in delicacy, freedom from attack by acids, and length of life, but also on account of their simplicity of action. By means of pipes connecting the weighing scales with each tank, the required amounts of each acid are weighed in separately, and by means of a stirring arrangement connected with the interior of the scales, the contents are slowly but thoroughly stirred for a considerable time (about three-quarters of an hour) to insure complete mixing. A sample is

1. U. S. P. 164260, 1875.

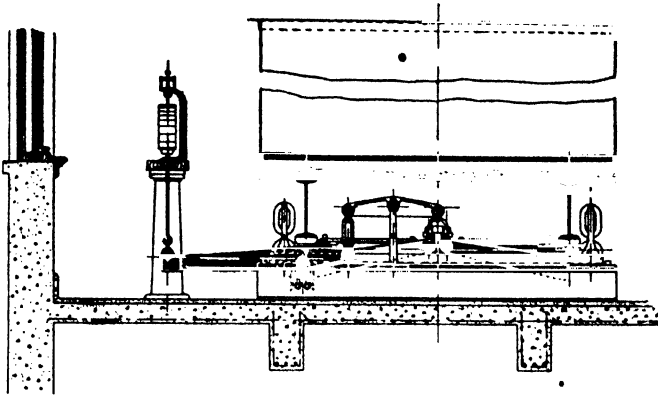


FIG. 119.—FAIRBANKS SCALE

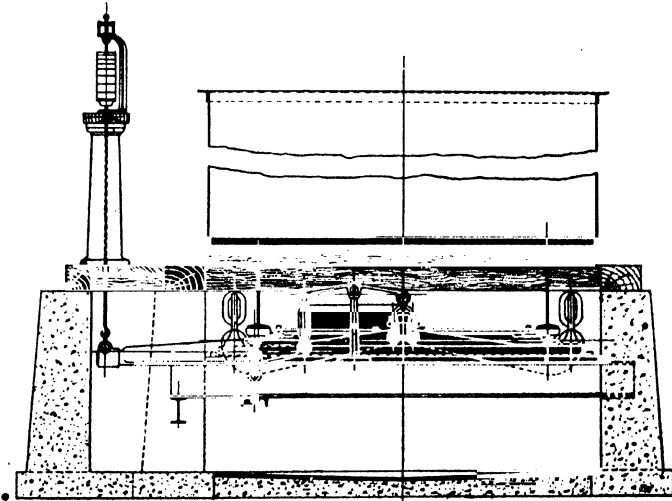


FIG. 120.—FAIRBANKS SCALE

These scales, shown in Figs. 119, 120, are designed especially for the weighing of corrosive fluids, as nitrating acid. The scales can be constructed so as to admit of mechanical stirring devices in the mixing tank, without impairing the accuracy—which is usually about 5 lbs. in a 60,000 lbs. charge

then withdrawn and subjected to analysis, any further adjustment of strength being made in the manner just described. From the scale tank the acid is run into the nitrating centrifugals or pans by gravity as required, or another storage tank may be provided, in which instance a day's supply ahead can always be kept. Nitrating houses and fortifying houses are usually arranged on a hillside if possible, in order to take advantage of varying heights for gravity flow of acids. The acid tanks ("eggs") are usually constructed of high carbon iron, the Bessemer steel tanks of G. Mowbray having apparently not come into use.

It is almost superfluous to point out that when nitric acid is being mixed with sulfuric acid or with oleum, or during the regeneration of waste acids from oleum or nitric acid, rise of temperature is always accompanied by the appearance of nitrous fumes. It is imperative, therefore, that the weighing and mixing vessels should be as tightly closed as possible and the containers provided with an efficiently working exhaust pipe, that the deleterious fumes may be reduced to a minimum.

Inasmuch as the presence of nitrogen oxides in nitrating acids is decidedly objectionable, it has been found expedient, wherever possible, to house in acid tanks of all kinds, it having been found that exposure of the tanks to the sun tends to decompose the nitric acid with an increase in evolution of nitrogen oxides.

Nitrocotton Spent Acid Recovery. Gretna Practice. The following method indicates the high efficiency with which the recovery of nitric and sulfuric acids has been developed in England, as exemplified by H. M. Factory, Gretna (Dornock Area).

The spent acid is run into a cast iron still heated with a gas fire, and the nitric acid in the spent acid distilled over into a condensing system. The residual sulfuric acid in the still is then removed to a concentration plant.

The spent acid storage consists of a number of cylindrical, mild steel boiler tanks of the usual type, built upon brick piers above the level of the stills in the house, so that all charging of the stills is by gravity. The boilers are preferably inclined so that one end is two inches lower than the other in order to allow solid impurities to flow towards the sludge outlet. At the opposite end and on the floor of the boiler is the acid outlet, into

which fits a cone plug controlled by a lever and chain. The run-off is supplied with a Quinan valve in addition to a plug valve, and is connected to a three-inch mild steel acid main. Each boiler is equipped with a gauge glass, and is capable of holding 89 tons spent acid of sp. gr. 1.68. In the United States the almost universal practice is to use Everlasting acid valves, the acid boilers containing up to 175 tons (in this instance short tons) of used nitrating acid.

The boiler is provided with a man-hole on the top, surmounted by a tripod supporting a dipping rod. At a depth of 6' 6" an overflow pipe runs common to all boilers, and similarly a common 3" main feeds a main of the same diameter, which runs the entire length of the still house. From this latter, each still is charged.

The stills are arranged preferably in batteries of three, and each consists of a cast iron, cylindrical vessel with a spherical bottom, the body being 2", and the bottom 3" thick. A satisfactory size has been found to be, total depth, 7', diameter, 6' 9", width of lid 3' 4", and width of lid to man-hole, 1' 8". Each still, for best results should be enclosed in a brick setting. The dome cover has a flattened top, and is attached to the pot by means of a rust joint, the lid being bolted on to the top of the dome cover. The lid is recessed to a depth of 2½" and 12" diameter round a circular hole 8" in diameter. Into this hole is fixed the still head. The man-hole lid is perforated with a hole 3¼" in diameter, through which passes a 7' dip pipe reaching to the bottom of the still, and also with a 1" hole to allow an air pipe being fixed.

The still is said to take a charge of seven tons of spent acid, and when in continuous use the nitric acid can be distilled off in nine hours, the complete cycle from starting one charge to the next being twelve hours, thus allowing two charges per day to be worked.

Hot producer gas is used for firing, supplied by a flue 3' 6" deep and 3' wide, running the full length of the still house. Each still is supplied with its own 4" control gas valve, which sits on the top of the flue and at the side of the door of the combustion furnace. Heating of the still is controlled within narrow limits by this arrangement. The gas is mixed with air, the combustion

takes place within a firebrick chamber 22" x 48" x 24". The products of combustion are removed through three circular flues built round the body of the still, connection between each being by means of vertical shafts placed in front of and behind the setting, with the result that the gases are forced to pass directly round the body of the still before emerging into the adjacent horizontal flue. Each of these flues is provided with two explosion doors at the front of the setting, and two behind the setting.



The waste gases leave the setting by means of a long vertical flue running down from the topmost horizontal flue to a waste gas flue 3' 6" x 3' wide, which runs underground behind the whole length of the house. In the middle of the waste gas flue a large flue runs off at right angles to the chimney stack, the latter being built of steel plates riveted together, is 120' high and lined with firebrick the first third of its height.

A lead pipe 2½" internal diameter conveys the spent acid from the charging main to the still, and also delivers the residual acid at the end of the distillation into the launder leading to storage of weak sulfuric acid.

The connection between this pipe and the 3" feed main containing spent acid consists of a 1½" lead U-bend, with two plug cocks situated in front of the latter. The charging and blowing pipe is supported on channel iron, and continued out of the house to the launder above mentioned. Between the launder end of the charging and blowing pipe and the inlet from the U-bend is placed a 3" plug valve, which is always closed during distillation and charging. The other end of the charging and blowing pipe is bolted to a swan-neck connection of the "dip" pipe in the still. This pipe is of cast-iron or Narki metal, the latter, although more costly in initial outlay, is finally cheaper than cast-iron, because of its much longer life. A cast-iron dip pipe 7' 2" very easily chokes with sulfate, and corrodes rapidly. The still is charged through this pipe, the contents at the end of the distillation being discharged through it.

The launder is for the conveyance of residual sulfuric acid to the weak sulfuric acid storage, runs the whole length behind the house and about 20' away from it, being supported on a wooden trestle and consists essentially of a leaden trough suspended in water, contained in a wooden launder. It is built in

60' sections with a fall of 1 in 120 and the acid is delivered into it by the $2\frac{1}{2}$ " blowing pipe connected to the dip pipe already described.

The greater length of the launder is  shaped and the remainder is . The half round shape gives much better results by reason of low maintenance cost, as compared with the other. Each 60' length is suspended in its own water bath section, with independent water supply and overflow scuppers, the water used being waste water from the acid mixing plant, but in the event of this failing, there should also be direct connection from the water service main. In the water-cooled portion of the launder the sulfuric acid is cooled from 200° to 100°, and reaches the storage tanks at 70°-80°.

The still head is a two-way piece with internal diameter of 8" and made of Narki or other acid-resistant metal, fixed to the 8" opening in the lid of the still with cast-iron collar plates bolted down at its base. The vapors pass up into the still head, and are shunted through the bend into the uptake. The short vertical extension of the still head is used for dipping, and to allow the fixing in of the sealing plug when the contents of the still are ready for discharge at the end of the distillation.

The sealing plug is a flat disc of cast-iron, having an elevated rim on its circumference which fits into a groove running round inside the bottom of the still head, the object being to totally seal the vapor outlet from the pot in order to allow the residual acid to be blown out of the still by means of compressed air. The acid is blown back through the dip pipe into the launder. The compressed air is allowed to enter the still through a small $\frac{3}{4}$ " pipe screwed into the man-lid, the supply of air to the stills being brought from a common air main running the whole length of the house, by means of individual 1" pipes. The pressure of air in the common main is kept at 10 lbs. per square inch, being reduced to this from 80 lbs. per square inch in the main air line.

The uptake is the vertical continuation of the still head, and essentially a straight pipe 8" in diameter and made of Narki metal. The uptake is continued with a bend which joins to the end of the cascade; the latter being inclined to the vertical at about 70°, and is built up of a series of earthenware pipes 8" in diameter, of which there are 5 in number, about 3' 6" long. It

is built upon a wooden trestle supported at each end, and runs from the top of the still to the condenser staging. Underneath the whole length of the cascade runs an earthenware gutter for the purpose of catching drips from cracked pipes or leaky joints.

In the Hart's condenser the nitric acid vapors pass through glass tubes cooled externally with cold water. The condenser consists in the main of six standards, 78 glass tubes and a double-socketted "S" bend. The gases after travelling the entire length of the cascade are directed into the "S" bend, which is an earthenware pipe 8" in diameter, supported on brick piers at a point just below the condenser platform. Into the sockets of the "S" bend are jointed two base pipes (Narki metal) which lead up through the floor above the "S" bend. Two standards 6' in height are then erected vertically, and in connection with the base pipes. At a point 6' 6" away and directly opposite, are arranged two other standards of the same height and material; the latter being known as "back standards."

The front and back standards are connected in parallel by means of glass tubes, 52 in number or 26 in each set, each of 1 1/4" diameter, and inclined at an angle so that condensed acid may run back to the front standards. They are clothed with good absorbent cloth, threaded S-wise through the stack of tubes. Water is fed from an aluminium distributor running parallel with and situated above the top glass tube, with the result that the water flows down over the absorbent cloth, thus exposing each glass tube to a cooling surface. The vapors are condensed, and owing to the fall in the glass tubes, the condensate flows towards the front standards and there falls down into the S-bend.

The remainder of the gases which are not condensed in the first two units running parallel, pass from the glass tubes into the first and second back standards, the only outlet of which is placed in the top, the other end of the standards, which rests on the floor, being closed. This marks a difference from the front standards. The gases entering the back standards and leaving by the top meet in a junction piece of 6" pipe leading in to the top of a third back standard. The gases from the third back standard are led by 26 glass tubes to the third front standard.

The tubes of this third and last set are clothed with absorbent cloth, and water is fed over them as over the other sets.

Further condensation takes place, the condensate running in the same direction as the gases, whereas in the first two units the gases and condensate flow in the opposite direction. A point of difference between the third front standard and the other two is, that the former has an opening at the top which is connected to a fume main to be described later. The surplus water running from each of the three stacks of tubes falls into an earthenware pipe leading to the drain.

The acid condensed is run off into a main through what is known as the "still watcher." That collected in the S-bend is made up of what has condensed in the cascade by air cooling, also some condensed in a similar manner in the body of the bend and the major portion from the glass tubes running in the first two units. But the acid condensed in the third standard does not run into the S-bend. In this case, the acid leaving the ends of the tubes with the third standard falls to the bottom through the base pipe which pierces the condenser platform, and collects in a small cylindrical catch-piece 6" diameter and runs off to the still-watcher, where it joins with the acid from the S-bend.

The still-watcher is a "U" piece of earthenware with a "T" piece fixed on one end and a saucer fixed to the other end. The "T" piece receives the acid from the S-bend of the first two condenser stacks, and the acid from the small catch-piece of the third condenser stack. The acids are mixed and flow by gravity through the other limb of the "U" and overflow into the saucer, which has two run-offs 1" diameter—one to the strong and the other to the weak acid main.

It will be observed that the U-bend forms a natural seal, and also that the open end of it affords a convenient place for taking the gravity of the distillate. The one-inch run-offs are provided with earthenware cocks, enabling the distillate to be run into the strong or the weak main as desired.

The fume main is made of earthenware pipes 9" diameter, well supported on a good wooden trestle, and runs the whole length of the house in front of each set of condensers. The main is connected with the condensers through an inverted "U" pipe 4" diameter. There are 30 such connections, each provided with a damper, so that any still may be shut off from the fume main if necessary. The main falls from each end of the house towards

the middle, where it branches off into a 9" main running directly to the absorption system.

The strong and weak acid mains are of 3" earthenware pipes, joined together and resting in wooden brackets, and are supported on a brick pier, with a fall of 1 in 120. They lead to the strong and weak acid receivers respectively.

The 3" main conveying strong acid delivers into a main of the same diameter which runs immediately behind, and the full length of the strong acid receivers. From this latter main five 3" branches run off at intervals between each two receivers and deliver into coolers, the latter consisting of a 2" lead coil, 60' in length, immersed in a bath of running water. There are five such coolers, and the coil of each terminates in a "T" piece so that no one coil will serve two receivers. It has been found, however, that a 2" coil is insufficient to carry the delivery of a 3" main when 22 or more stills are running, and in order to overcome this difficulty two additional coolers are required, allowing two coils to be used to fill one receiver.

The strong nitric acid receivers are six in number and are constructed of lead, strengthened with timber battens and iron hoops with lead cover, supported by covered iron rods. They are 8' 3" in diameter and 2' 9" deep, carried on a reinforced concrete floor on brick pier at a suitable height to give a gravity feed to the mixing station, each receiver having a working capacity of about six tons of strong nitric acid. The content of each receiver is run off at the bottom through a 2" earthenware cock into a 3" lead main. Samples can be drawn; the receiver can be dipped through a hole 5" in diameter in the lid situated near the edge, compressed air being used to agitate the contents before sampling. Each receiver is fitted with a 4" earthenware fume pipe, having a damper, the fumes being led into the 9" fume main previously described.

The weak nitric acid receivers are supported on a concrete floor built on brick piers at a height of 8' 4", of earthenware, and each has a working capacity of approximately 0.7 ton of weak acid at 1.4 sp. gr. Each receiver has a diameter of 3' 2" and a depth of 2' 6", with a 2" fume outlet connected to the 9" fume main. The 3" acid main running to the weak receivers has ten branches, each of which feeds one receiver, the outlet from each

receiver running into a common 2" earthenware main. The inlet and outlet cocks are 2" plug type.

For the purpose of collecting drips or washings from receivers, etc., an earthenware egg is placed on the ground floor of the plant, being filled from an earthenware main in connection with the various points of the house. The capacity of the egg is 77 gallons, and when full is discharged by means of compressed air at 10 to 15 lbs. pressure, the discharge being a 2' earthenware pipe which branches off to both the strong and the weak receivers, and into which the contents of the egg are blown according to strength.

In construction, the absorption system is almost the same as that used by the retorts. The packing of the towers belonging to the stills is different from that in the retort towers, quartz being used in the latter but Accrington rings in the former. These latter consist of a hollow cylinder, punctured at each end to give a cartwheel design, which fits loosely into a ring 4" diameter and 3" long. The whole is made of acid-resisting earthenware, and the rings are packed end upon end. The earthenware ring packing has the following advantages over quartz packing:

1. Proportionally greater free space
2. Proportionally greater wet surface
3. Greater uniformity
4. Less liability of choking
5. Small lateral pressure on the tower body

The spent acid to be distilled has an average sp. gr. of 1.680 at 15°, of a pale straw color, gives off nitric acid vapor on exposure to air, and contains a slight amount of sludge which is chiefly ferric sulfate. Its average composition by weight is: HNO_3 10.3%; H_2SO_4 60.9%; H_2O 18.8%.

The action upon mild steel, lead or cast-iron at ordinary temperatures is not excessive and it may be stored in boiler tanks of mild steel with safety.

The storage of the spent acid is at such a height that all stills can be charged by gravity. The storage boilers are sludged periodically and kept well painted. All valves, both inlet and outlet, are kept well greased, and turned at least once every day. The staging and steps around the storage boilers are well painted and also well illuminated for dipping, etc., during the night. A gangway runs across from the charging platform of the house,

so that in the event of valve trouble speedy communication is possible.

From the dimensions of the pot, the tonnage or capacity is found, and on this plant a charge of 4' 9" of spent acid is approximately seven tons by weight. When the charging valve is opened the acid runs in with a force dependent upon the head, twenty minutes being taken as the average time required to run in a charge. The pot is dipped at intervals with a copper rod having a ring marked at a point 4' 9" from its bottom end. The rods are checked in measurement weekly.

Iron rods have been tried, but overcharging frequently occurs by reason of "sweating" on the surface when the rod is put into the still and giving a very indistinct mark. More recently an electric charging appliance has been used which measures the charge with a "dry" dip and rings an alarm bell when the still is fully charged. When the charge has been run in, the still is sealed at the still head in readiness for distillation. Two stills can be charged at the same time, but then the charging time is lengthened from twenty to thirty minutes.

After distillation is complete the fire is drawn and the cover from the still head removed. The blowing plug has been prepared, and this is immediately screwed into position by means of a screw clamp. In preparing the blowing plug, it is necessary to provide it with a suitable packing that will withstand the temperature and the acid fume, and it has been found that asbestos cord is the best for this. One piece, if properly handled, is sufficient for twenty or more blows. When the plug is in position the air pipe is connected up, the still and compressed air turned on at a pressure of 10 to 11 lbs. per square inch. The supply should be perfectly free and steady, and the dip pipe clear of sludge. As the pot empties the rate of discharge of the residual acid somewhat diminishes, due to increased lift as the acid level in the pot lowers.

The fire may be put on when the still is half charged, and a good brisk fire kept until distillation commences, which is on the average, 2½ hours afterwards. The fire is lessened somewhat when distillation has commenced, but care should be taken in avoiding decrease of temperature. It will often be necessary to increase the fire towards the end of the distillation rather

than reduce it. Without good firing dependable results are difficult to attain. A slow, inactive fire gives a very unsatisfactory distillate, large quantities of nitrous acid being formed, and the distillation becoming unduly lengthened.

Vapors begin to pass over at 90° containing much of the nitrous acid from the spent. At 135° a good distillate is obtained, and it is at this point that most of the HNO_3 is obtained. The temperature of the vapors passing up through the uptake gradually increases and the HNO_3 content correspondingly diminishes until at a temperature of 145° – 150° the distillation is complete. This point, however, is not determined by temperature, but by taking the gravity of the distillate. When the gravity of the distillate has fallen to 1.300 the distillation is considered complete.

The whole of the distillate from a charge is run into the same receiver, and the resultant is an acid of average strength of 89.5% HNO_3 . Each seven-ton charge of spent acid gives approximately 1.4 tons of HNO_3 .

The control of the condensers is an important item, and care is specially required in water feed. Spent acids from cotton nitrations contain an appreciable amount of nitrous acid. It is, therefore, more economical to condense HNO_3 only in the condensers and allow the nitrous acid to pass on to the absorption system. This can be controlled on the condensers only, and is of much importance. To successfully carry out the elimination of nitrous acid to the maximum, it is necessary to run the condensers as hot as consistent with efficient condensation of the nitric acid throughout the whole distillation. More water is required on the condensers in the middle of the distillation than at the beginning or at the end.

All gravities of the distillates are taken on the "still-watcher," or gravity platform which runs directly underneath the condenser platform. The gravity man informs the fireman when a still has finished; preparations are then made to "blow" the still and clean the gas valve. As soon as a receiver is filled, a sample is drawn for analysis, but it is essential that the contents of the receiver be well agitated with compressed air before being sampled. This serves the double purpose of removing nitrous acid and mixes

the contents. The sample is then forwarded for analysis.

Owing to the much greater amount of oxidizable nitrogen compounds entering the still absorbers as compared with those of the retorts, a somewhat different method of control is required. The Pohle air lift works much faster, and ensuing oxidation reaction is more intense, while the yield of HNO_3 is considerably greater. The gases enter during the summer months with an average temperature of 30° and by the time they have reached the third tower in the set, the temperature has risen to an average of 50° . The strength of acid in the towers varies between 9% and 10% of the total HNO_3 made, and contains on the average 0.1% nitrous acid.

Denitration of Waste Acids. The prodigious amounts of nitric and sulfuric acids used at the present day for nitration of cellulose and other bodies, are, in keeping with modern ideas of chemical conservation, re-energized, rejuvenated and fortified for re-use, so that in large scale commercial nitration processes at the present time, only 2% or 3% of the nitric acid is ultimately lost. The economical fortification of exhausted nitrating mixtures has reached a high state of perfection, due to the researches of O. Guttman, H. Chardonnet, C. Jahn, V. Vèder, R. Evers and others.

In 1886 O. Guttman and M. Abelli carried out exhaustive experiments on the recuperation of waste nitrating baths and the regeneration of the nitric and sulfuric acids contained therein in a form and purity suitable for re-use. Formerly the custom was to increase the nitric in the spent acid for one or two re-nitrations, but the increment of water split off in the esterifying processes, and the rapid accumulation of impurities soon unfitted the mixed acid for use, when it was discarded. This particularly was the case when highly nitrated organic bodies were being prepared, where also the waste acids from a higher stage of nitration were employed in the preliminary nitration steps. This method of nitrating acid conservation has its limitations, and is applicable economically in comparatively isolated instances. Especially is this true when some of the products of nitration or subsidiary products formed in the normal esterification process are soluble in the nitrating fluid.

The spent acid is denitrated for the recovery of the nitric

and sulfuric acids contained therein. In general, these processes depend in the main upon the extraction or elimination of the nitric acid portion by some fractionation process involving distillation, the temperature being raised either by external heat as by pressure steam distillation, or more usually upon the introduction of jets of dry steam, hot anhydrous gases or dry air. Denitration proper is usually performed in high, acid-proof towers of refractory material, the interior being filled with small pieces of acid-resisting material especially manufactured for this purpose.

The denitration installation is based essentially upon the principle of the introduction of a slow stream of waste acid at the top of such a tower which gradually flows downward, being impeded by a contrarily moving stream of steam or hot air which enters at the bottom of the tower. By this method the volatile acid (nitric) vaporizes, leaving the non-volatile acid (sulfuric) behind, to be purified and separated from dissolved and insoluble impurities by a separate process.

The average composition of the waste acid from nitrocellulose manufacture will vary as to whether hand, centrifugal or displacement systems of nitration have been employed, and as to whether a high or lower nitrogen-containing nitrocellulose has been produced. In general the waste acid from the nitrocellulose manufacture will average about 75% sulfuric acid, 12% nitric acid, and the balance water. When the mixed nitrating acid has become either so weakened in nitric acid or contains too much cellulose in solution and suspension, the mixed sulfuric and nitric acids are separable by some process involving distillation.

In the older process of H. de Chardonnet¹ the waste acid is introduced into a still which is heated to about 170°, from which fairly pure nitric acid containing considerable quantities of nitrogen oxides in solution, distils over. The sulfuric acid, which still contains some nitric acid then flows through a pipe line to a second still in which the balance of the nitric acid is distilled at a temperature of 200°-210°, giving a more diluted nitric acid. The sulfuric acid, concentrated to about 62° Bé., sinks to the bottom of the still and is removed by a syphon or

1. D. R. P. 56331, 56655; abst. Mon. Sci. 1905, **63**, 321; Ber. 1891, **24**, 1004; Wag. Jahr. 1891, **37**, 1113; Zts. ang. Chem. 1891, **4**, 466.

other suitable means. This method has given general satisfaction.

Where large quantities of nitrogen oxides and nitrous vapors are to be recovered, either from the waste acids from nitration or from other sources, a combination of several plate towers is employed, one of which is preferably erected above the others, so as to feed them by gravity with the weak acid produced. In this manner with careful manipulation it is possible to bring the recovered nitric acid to a strength represented by a gravity of 1.40.

H. Pauling¹ places nitrosulfuric acid in the anode compartment of an electrolyzer, dilute nitric acid being used to fill the cathode compartment. The nitrogen oxides evolved at the cathode are transferred to the anode compartment.

According to G. Lunge,² the following process for the recovery of nitric acid from the waste acids produced in the manufacture of nitroglycerol and nitrocellulose, as carried out at Haylem works very well indeed. The waste acid is denitrated in a small volvic column, standing in a strong leaden socket, with an overflow about eight inches from the bottom. The steam pipe must not end free in the column, but within the liquid, say six inches below its level, so that the steam rising from the liquid effects the denitration. The operation is commenced by putting water into the lead socket and passing in steam until the column is hot. Only then the feeding with the waste acid is started and is conducted in such a manner that at the bottom sulfuric acid of 74% to 75% strength issues at a temperature of 160° C., in which case the denitration is perfect. The nitrous vapors pass first through four empty receivers, for the purpose of cooling, then successively through five Lunge towers, about 6 feet high, and then through eight receivers, charged with six inches of water each. The towers are fed very slowly with water, the holes in the covers being plugged up with wood in such a manner that the water trickles down in drops. On top of the first tower one of the holes is left open in order to draw the necessary air. Thus the towers yield nitric acid of 57% to 64% HNO₃, inclusive of 1.5% N₂O₄, on the average of sp. gr. 1.40. The water in the receivers is left there until the specific gravity reaches 1.37.

1. U. S. P. 898390; abst. J. S. C. I. 1908, **27**, 986. C. A. 1909, **3**: 362. See also J. Pratt, E. P. 14173, 1884. Zts. Schiess. Spreng. 1917, **12**, 57.

2. G. Lunge, "Sulfuric Acid and Alkali," 198.

This plant denitrates approximately 10 tons of waste acid per diem.

In the system of denitration of waste acids, especially applicable with the nitration of glycerol, H. Lemaître¹ superheated steam at a temperature of at least 300° is injected into the lower part of the denitrating tower. With a cast iron injector a temperature of 400° may be used. Pre-heated air also gives good results, the necessary water vapor for denitration being in this case derived from the dilute acid in the lower part of the tower. The upper part of the tower is sprayed with dilute nitric acid (15°–20° Bé.), which affords part of the water for the denitration; also the distribution of this nitric acid causes absorption of heat and consequent cooling of the upper zone, thereby avoiding dilution of the recovered nitric acid by holding back the water. By proper regulation of the steam current and spray the condensed nitric acid is kept at 38°–40° Bé. and the sulfuric acid containing only 2.5%–3.0% nitrosulfonic acid is obtained at the base of the tower. On concentration of this sulfuric acid to 96%–97% practically all of the nitro products are driven off. It is shown that all nitric and nitrous products in waste acid tend to the formation of nitrosulfonic acid, rapidly by concentration with heat alone, or gradually on long storage at ordinary temperature.

More recently² has appeared the process of A. v. Vajdady for the recovery of waste acids from nitrocellulose manufacture. Part of the waste acid is recovered by subjecting the nitrocellulose to a preliminary pressing, most of the remaining acid being then removed by hydraulically compressing the nitrocellulose, these two operations, as well as the ejection of the compressed nitrocellulose, being carried out as part of a continuous cycle. The apparatus comprizes a press-table provided with perforated cylinders, in which plungers operate. The three operations (light pressing, heavy pressing and ejection of compressed material) are carried out simultaneously in successive cylinders, and by rotating the table the material is subjected to each operation in succession; the cylinders have movable plates below to retain the material during the movement of the press-table. The process

1. Mon. Sci. 1913, **78**, 217; abst. C. A. 1913, **7**, 2118; abst. Zts. Schiess. Spreng. 1914, **9**, 9, 30, 48; C. A. 1914, **8**, 1508.

2. D. R. P. 313046, 1918; abst. J. S. C. I. 1919, **38**, 879-A. Cf. R. Rogers, U. S. P. 176813, 1876. M. Engerls, D. R. P. 301550, 302255; abst. J. S. C. I. 1918, **37**, 345-A.

enables the waste acid to be expressed from the nitrocellulose in a few seconds without risk of decomposition. The pressed material passes to a conveyor or direct into a pulping machine.

Where mixed acid is too weak for economical rejuvenation, but still too concentrated for discharge into effluents, the acid may be treated with scrap iron or iron filings until neutralization and reduction are practically complete. If desired, waste alkali, such as lime, soda or waste sulfite may then be added, and the mixture clarified by filtration if necessary, to obtain a clear liquid suitable for discharging into a stream or the sewer.¹

In the recovery of acids used in nitration according to the method devised by J. Skoglund,² and especially designed for the separation of acids from products such as nitrocellulose or nitro-starch, the product is successively treated with different portions of acids each more dilute than the preceding, and finally with water. This avoids any danger from overheating, such as might take place if water were added to the strong residual nitration acids without the intervening displacement with weaker acids. In treating nitrostarch, the latter may be placed on a "filtros" plate, the strong acid drawn off through the plate, replaced by acid of 56° Bé., then with acid of 42° Bé., and then with water while the temperature is maintained below 20°. The acids may rapidly be removed through a "filtros" plate by the application of suction.

According to C. de La Condamine,³ nitric acid may be advantageously concentrated by introducing it simultaneously with strong H₂SO₄ into a tower, suitably packed, through the bottom of which steam is injected. HNO₃ is distilled and flows upwards, leaving the tower at the top, together with a certain proportion of the H₂O. Most of the latter, however, is absorbed by the H₂SO₄ which is withdrawn at the bottom in dilute form. De-

1. British Dyes, Ltd., J. Turner and H. Dean, E. P. 127039, 1917; abst. J. S. C. I. 1919, **38**, 555-A; C. A. 1919, **13**, 2451. British Dyes, Ltd., Davidson and J. Turner, E. P. Appl. 17871, 1918.

2. U. S. P. 1311017; abst. C. A. 1919, **13**, 2451. See J. Charlton, E. P. 25935, 1912.

3. L'Ind. chim. 1918, **5**, 153; abst. C. A. 1919, **13**, 2664. Dynamit Akt. Ges., D. R. P. 254754, 1909; abst. C. A. 1913, **7**, 1291. Delpy, E. P. Appl. 11240, 1916; J. S. C. I. 1917, **36**, 79. Matheson, E. P. Appl. 1730, 1919; abst. J. S. C. I. 1919, **38**, 94-A. E. Allary (Bull. Soc. Chim. 1887, (2), **47**, 102) has found that the waste acid from the manufacture of guncofton may be regenerated by distilling after filtering through quartz, or more preferably, that it be used for the manufacture of nitric acid from sodium nitrate.

nitration of nitro-sulfuric mixtures is accomplished in a similar tower of lava stone or acid-proof metal and packed with acid-proof brick, quartz or other suitable materials. Suitable condensing apparatus is provided. Large sectional area is of considerable importance, as small tubes increase rapidity of the flow of the gases through the apparatus, so that insufficient time for the condensation to take place is allowed. Tubes of elliptical section are advantageous. The condenser recovers only 80% to 90% of the HNO_3 distilled, the remainder being recovered in absorption towers or Kaltenbach apparatus. The latter consists of stoneware tubes, alternately empty and full of water, through which the gases bubble. 45% HNO_3 can be obtained. Absorption towers recover the uncondensed acid and oxidize NO_2 to HNO_3 . Five to six towers constitute a system. Towers are made from earthenware sections and are generally 90-100 cm. in diameter and 5-6 m. high. An available surface of 40-50 sq. cm. is sufficient to recover the nitrous gases resulting from the distillation of a metric ton of HNO_3 in 24 hours. The recovered acid flows from each tower back to the preceding one while the last tower in the system is drowned with water, the quantity of which is so regulated that the recovered acid does not fall below 32° Bé. The oxidation of NO_2 to HNO_3 is accomplished by means of the air which filters into the system. Oxidation is never complete, due to the reversibility of the reactions. The theory of the concentration of HNO_3 by this method is described in detail and curves are plotted to show the effect on the concentrated HNO_3 of variation in the quantity and strength of the HNO_3 , H_2SO_4 and steam introduced into the tower. A distillation curve is also developed. The per cent. HNO_3 in the concentrated acid is dependent primarily on the proportion of H_2O in the mixture. In denitrating a nitro-sulfuric mixture, the water content should not be more than 18% to 20%, if it is desired to obtain strong HNO_3 . If the quantity of H_2SO_4 is increased, the strength of the recovered HNO_3 is unchanged, but if the strength of the H_2SO_4 is increased, the distillate will contain a larger proportion of HNO_3 . An increase in the quantity of steam used will not affect the concentration of the HNO_3 obtained, but will result in the recovery of more dilute denitrated H_2SO_4 . Theoretical calculations indicate that 0.45 kg. of dry saturated steam at 3

kg. absolute pressure and 133° temperature will concentrate 1 kg. of 50% HNO_3 to 0.58 kg. of 86% HNO_3 , producing at the same time 3.87 kg. of 71.3% H_2SO_4 , introduced along with the HNO_3 . Thermal calculations show that the heat generated will be sufficient to accomplish the ebullition of the acid. Superheating steam under good conditions will result in economy in the operation of the tower. The yield of HNO_3 should be 97% and the denitrated H_2SO_4 should not contain more than 0.06% HNO_3 .

In the method of E. Barbier,¹ the mixed acids are fed from

1. E. P. 11705, 1892. In Chem. Engr. 1909, **10**, 16, S. Frazier has given the structural details of a plant to manufacture from 60 to 80 tons of mixed acid per day.

M. Kaltenbach (Chim. & Industrie. 1919, **2**, 142; abst. C. A. 1919, **13**, 2109) has shown that although the concentration of HNO_3 can be accomplished by dehydrating it by means of H_2SO_4 , when the HNO_3 is very weak to start with, it is more economical first to preconcentrate by heating it to the boiling point and evaporating off the H_2O until the acid reaches 68% in strength, at which point it remains constant. The operation is carried on in a form of pot furnace, containing 7 pots, arranged in a cascade, each pot being connected to the next one by means of a small lateral tube, which permits countercurrent circulation of liquids and vapors. Heat is generated in a fire-box at the lower end of the furnace. A connection from the fifth pot, counting from the fire-box end, leads into a rectifying column, through which the hot HNO_3 vapors pass. The column is separated into 2 distinct parts. In the lower part, rectification takes place. The vapors are sprayed with weak HNO_3 , which flows down the tower in a carefully regulated stream and enters the distillation pot at the boiling point. The HNO_3 vapors, almost entirely denitrated, then pass into the upper portion of the column, where the last traces of HNO_3 are removed by spraying with fresh H_2O . The HNO_3 , thus recovered, is collected separately, cooled and may be used to irrigate the hypo-nitric towers. The H_2O vapors are removed by means of a barometric ejector-condenser, which also furnishes a means of overcoming the natural resistance of the apparatus. The partition, dividing the tower into two parts, prevents the mixing of the strong and weak HNO_3 solutions. The reservoir, feeding weak HNO_3 to the tower, also feeds the coldest pot at the stack end of the furnace. Dehydration or denitration must be resorted to, to raise the HNO_3 above 68%. Descriptions are given of the operation of the tower, and of the thermal balance of the denitration operation. The thermal relation of the various acids and the thermal efficiency of the process is discussed. Emphasis is placed on the importance of reducing the steam consumption to a minimum, thereby saving fuel and H_2SO_4 , reducing the total volume of acid treated and increasing capacity of the apparatus. The hotter the acids entering the tower the less steam will be required. Consequently, a heat exchanger is used to recover some of the heat contained in the denitrated H_2SO_4 , leaving the tower. A rise of 80° - 90° is obtained thereby, effecting a recovery of 20% of the total heat in the acid. The use of H_2SO_4 of higher concentration than 93%, while producing more heat on dilution, is not recommended, due to the increased cost. The quantity of heat leaving the system may be reduced by the use of preheaters for the denitrated H_2SO_4 , by the preconcentration of the weak HNO_3 and the use of an asbestos heat-insulating coating on the tower. It is advantageous to use superheated steam because of the greater heat contained therein. Other factors remaining constant, this results in an increase

a trough to a chamber where the liquid is heated by the gases evolved in an evaporating chamber, and introduced into the former by injectors. This preliminary heating practically removes the nitrous vapors which pass through a pipe into condensers and a tower. The sulfuric acid is then run through a trough into, and down a series of pans, heated by a furnace, the pans being supported on plates, and channeled ends provided for carrying off the liquid from a broken pan.

According to the process of D. Tyrer,¹ the acid is treated in the presence of an oxidizing agent with a substance capable of being nitrated to a nitro-compound insoluble in sulfuric acid. For example, spent nitrating acid containing 70% or less of sulfuric acid and 1%-10% of nitrous and nitric acids is introduced at about 110° along with air and toluene vapor, at the top of a tower packed with coke. The mixture issuing from the bottom of the tower is run into a separation tank, from which the purified sulfuric acid, containing less than 1% of nitric acid, is drawn off to the concentrators, while the residual mixture of toluene and nitrotoluene is used for making trinitrotoluene. Acid fumes and any toluene vapor escaping from the bottom of the tower pass through a pipe to coolers and scrubbers.

Evers Denitration Process. The invention of R. Evers relates to apparatus for de-nitrating nitrous sulfuric acid, and for

of 11.5% in the capacity of the tower, while reducing the H_2SO_4 used 18% and the steam injected 38.5%. For successful operation of the process, means must be had for controlling the various factors, variation in which tends to upset its equilibrium. Such factors are the weights of H_2SO_4 and HNO_3 charged in a unit of time, the concentration of these acids, the weight of the steam and its pressure and temperature, and the vacuum in the tower. Automatic appliances for keeping these constant for indicating their exact value at any time, and for changing each one independently of the others should be provided. Flow-cocks of special construction, provided with square or rectangular openings, are suggested as permitting a more exact regulation of the flow of the acid. Steam valves of the needle type are better than the seat type. Good results are obtained by connecting around the steam valve on the main line a by-pass controlled by a needle valve. An automatic air-admission valve regulates the vacuum in the tower at any desired point and at the same time admits air to the apparatus for the oxidation of the lower oxides. Recent developments have made possible the combination of the two operations in one and the same apparatus, and the reduction of the fuel consumption to a considerable extent, while decreasing by 50% the amount of H_2SO_4 required.

•1. E. P. 17541, 1915; abst. C. A. 1919, **13**, 1640; J. S. C. I. 1919, **38**, 340-A.

recovery of both the nitric and sulfuric acids.¹ The plant which is illustrated in Figs. 121-126, consists of the denitrating tower, a cooling arrangement, a condensing tower, and a firing place, the turrets being divided in superposed chambers by intermediate partitions, which are provided with one or more apertures, in which chambers the centrifugal mixing apparatus or filling bodies of tubes are provided. The apparatus consists of a mixing apparatus consisting of hollow cones equipped with plates, one cone being placed upon another, the walls being provided with apertures whereby the liquid blown in or the liquid dripping through the tower, sets the apparatus in rotation to effect an intimate mixture of the compound acid with the vapors blown in.

There is also provided bundles of tubes as filling bodies, consisting of series or groups of tubes of an egg-shaped section, the bottom of the tubes being bent in reverse direction for the purpose of deflecting the gases streaming through from their direction of movement, and to offer the maximum contact surface.

The essential features of the process is to insure most intimate admixture during absorption, and this is specifically brought about by reducing the acid to a very fine state of subdivision, by interposing obstacles in the path of the entering gases, and heating the waste acid to be recuperated. In addition to direct denitration, the waste acid is pre-heated preferably, even where organic residues and traces of nitro compounds are still present. A temperature of 160°-170° is maintained in the denitration towers by introducing superheated steam or air at several different places, the air being heated from the heat of the recovered sulfuric acid. Owing to the employment of hot air, the organic impurities in the waste acid are almost completely oxidized, with the result that the recovered sulfuric acid is practically water white and in a condition for re-use. The arrangement of the installation is such that the sulfuric acid obtained is clear and of a strength of at least 60° Bé. and the nitric acid substantially

1. U. S. P. 767335, 1904; abst. J. S. C. I. 1904, **23**, 866; F. P. 323397, 1902; abst. J. S. C. I. 1903, **22**, 495; E. P. 17316, 1902; D. R. P. 145743, 1903; 182216, 1902. In D. R. P. 176369, 1904, R. Evers describes a method comprising a vessel upon whose bottom are two coils, one within the other, through which the fluid to be heated is passed, alternately, so that the heat of the concentrated acid, which passed directly from the apparatus through a short tube set into the wall of the vessel is given up to the dilute acid to be next introduced into the midst of the vessel.

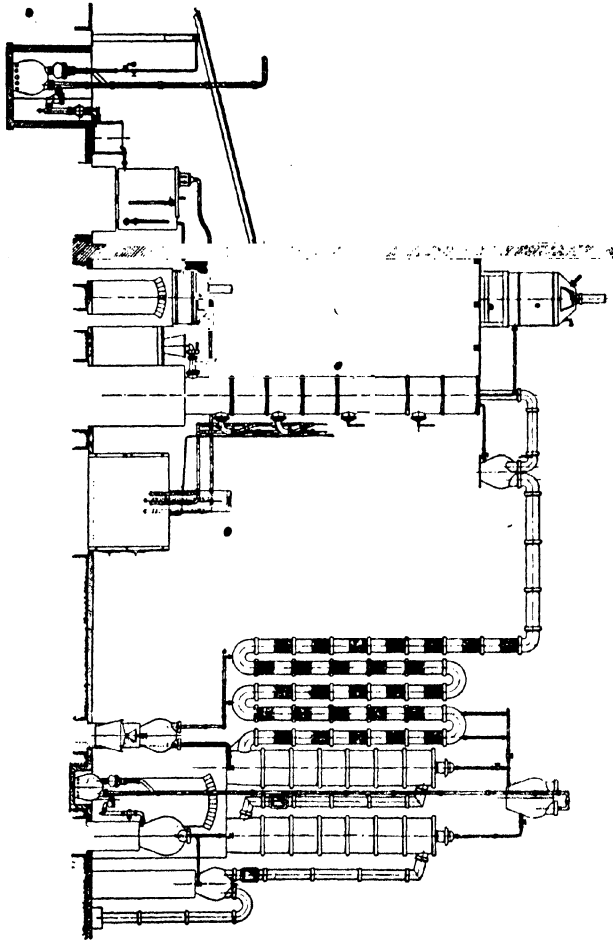


FIG. 121.—THE EVERS DENTRATING PLANT

colorless and of a concentration of 34° – 36° Bé., or where the strength is brought up to above 40° Bé. the acid is colored yellow.

The nitrous acid is passed down the tower "a," into which air and steam from the furnace "g" are introduced through the tubes "s." The sulfuric acid collects at the bottom and the nitrous gases pass through the condenser "b," and then up the absorbing column "c," down which water or other cooling or condensing liquid passes. The columns "a" and "c" are divided by horizontal partitions *h* having central apertures, into several compartments. In these compartments are placed a number of mixing devices *i*, and a number of tubes *k*; the latter are also placed in the condenser *b*. Each mixing device consists of a central perforated cone *l*, receiving mixed air and steam from the tubes *m*, and surrounded by an outer perforated cone *p* having ribs or plates *q*, *q*², which are shaped so that the liquid flowing

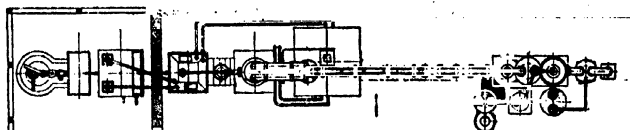


FIG. 122.—THE EVERS DENITRATION SYSTEM

down from the cup *q*² spreads over the whole surface. The liquid finally escapes from arms *r*¹, curved at their outer extremities so as to cause the outer cone to rotate. In one modification the outer cone has a screw-threaded outer flange running from the top to the bottom, and inclined vanes at the bottom. In another modification the outer cone is rotated by the entering gases acting against vanes at the bottom. The tube devices *k* consist of a double set of vertical tubes *t*, *t*¹, shaped as shown in the figures, and having their lower open mouths alternately turned inwards and outwards. The sulfuric acid passes over a mixing device *i*, similar to those described above, into the cooling vessel. The water in the nitric acid is stated to be vaporized in the column *d*. For denitrating the mixed acid, an intimate mixture of the air and dry steam with the latter is necessary. In the denitrating tower *a* the compound acid is separated into nitric and sulfuric acids.

It will be understood that the mixed acids enter the tower

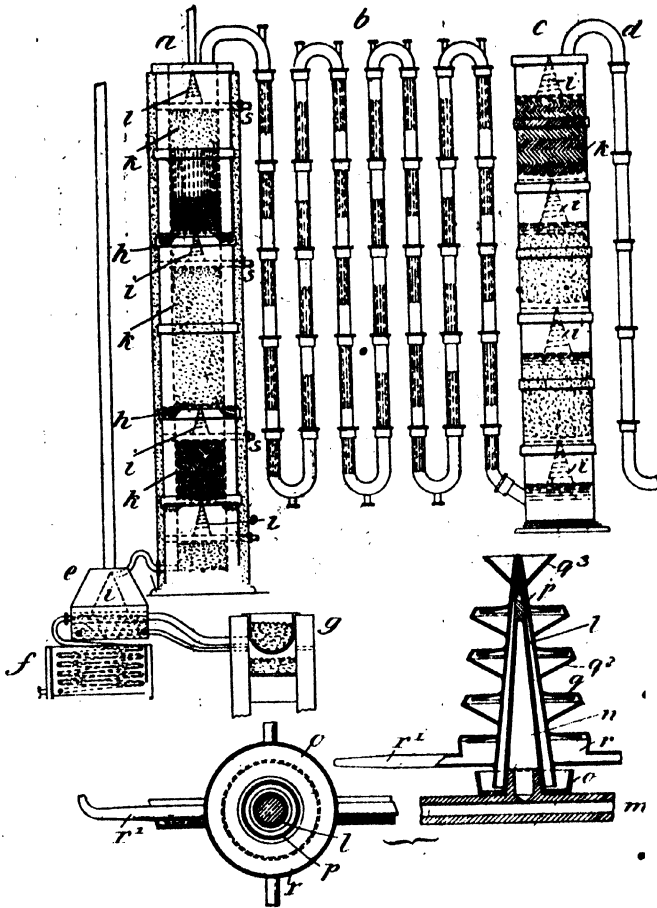


FIG. 123.—EVERS DENITRATING SYSTEM

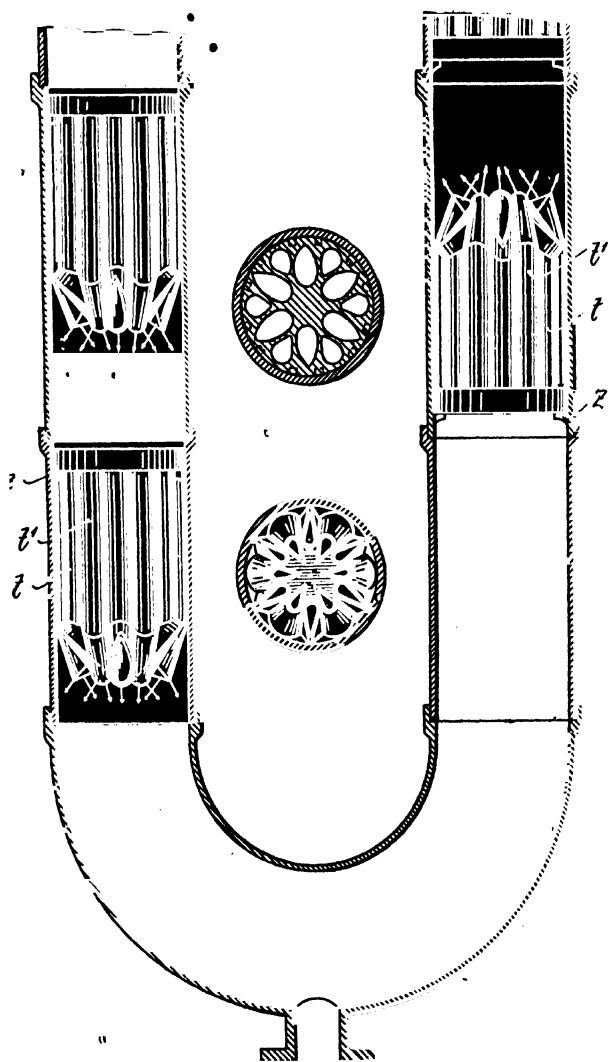


FIG. 124.—EVERS DENITRATING SYSTEM.

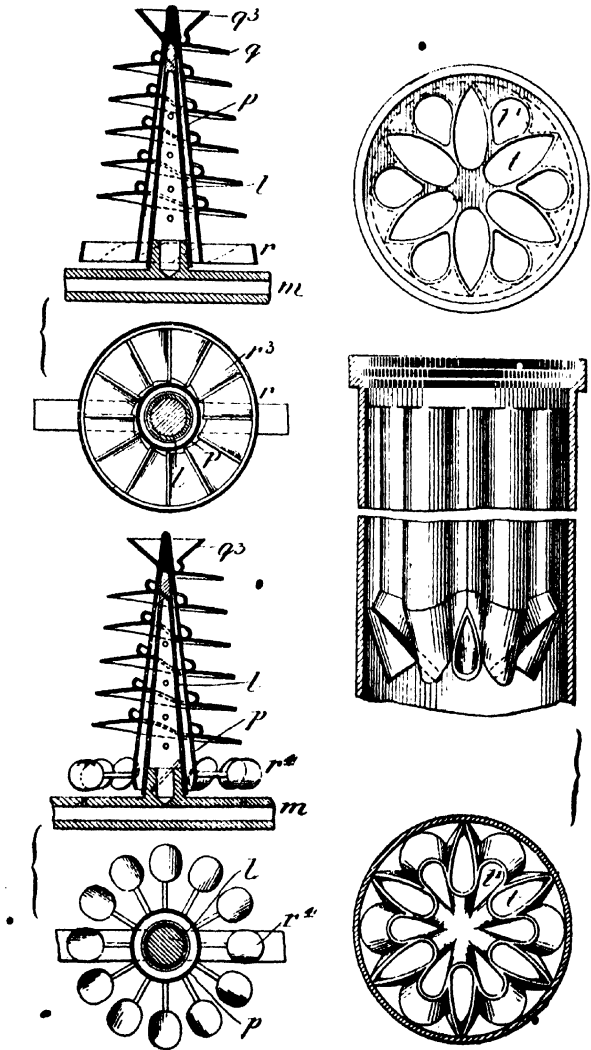


FIG. 125.—EVERS DENITRATING SYSTEM

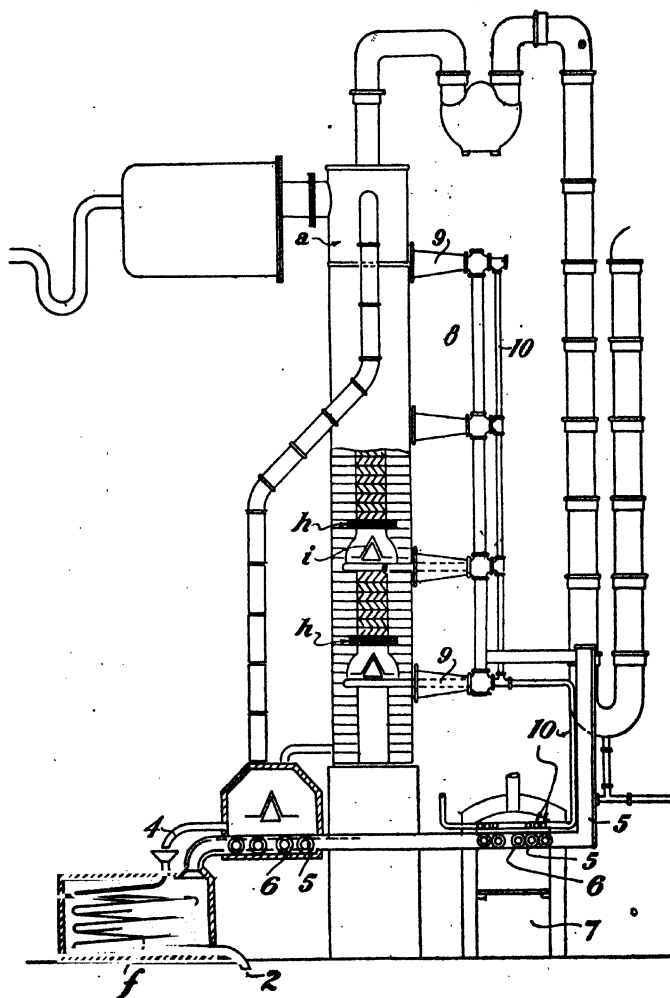


FIG. 126.—THE EVERS DENITRATION SYSTEM

at the top and are heated by rising gases and broken up into a spray by the filling checker-work and collected again on arches, thus effecting always a uniform interchange of heat. In the next lower compartment where the filling is of higher temperature, part of the nitric acid is driven from the mixture and this fraction shows a difference in composition and temperature. These unequal fractions or drops rejoin on the septum *h* and again mix into an acid of uniform composition and interchange of heat. This procedure is repeated successively in the following chambers of the reaction tower. In the lower chamber the mixed acid is heated so high that all the nitric acid is driven off.

After the acid in this chamber is dispersed and collected, it is again spread over the lower filling so that the remaining nitric acid is removed. By this fine dispersion it is possible to introduce the gases at about 400°, and thus to oxidize all the carbon into its oxygen compounds and to remove the water as steam. The hot gases are driven as quickly as possible through the lower chamber and filling bodies but with reduced speed through the upper chambers, in order to avoid too great a transfer of heat in the lower chamber and to accelerate it in the upper ones. By this method of repeated dispersion of the mixed acid and by the uniformity of the gas in the coils in the fire box in which it is heated by direct fire, the nitric acid is removed uniformly and not in spurts as with some of the older methods, either too soon or too late.

At the same time superheating or decomposing the nitric acid gases are to a great extent eliminated, and the transference of detrimental heat to the condensing apparatus is avoided. This heat and oxygen are saved. The mixing apparatus operates as follows: The acid enters at the top and the gases ascending from the bottom are deflected around a spiral apparatus which throws the acid against the walls of the vessel and thus mixes them. The regulation of the conditions of the denitration process usually does not call for an apparatus as complicated as that described by Evers, although the idea is excellent but unduly costly. This portion of the process, however, may be eliminated without detrimentally effecting the efficiency of the process as a whole.

The hollow chambers are quite necessary and indispensable for the uniform atomization and mixing of the acid with the

gases. This admixture of the gases and their re-dispersion brings them both into the most intimate contact and thus fulfils the prime function of the whole process.

The most striking feature of the Evers process is the strong preheating of the admitted air and steam, which are heated as high as possible in the same "firebox," which is maintained at a temperature preferably not lower than 400°. Furthermore, the construction of the "boiling tower" is not made of uniform diameter as at first, but gradually and uniformly widens toward the top, so that the velocity of the gases and the pressure is maintained regularly and with a predetermined uniformity. Also in the above description of the tower, the gases are allowed to diffuse or permeate and mix intimately with the acid. The whole procedure, in general, is quite simple, and its efficiency does not depend upon a number of fine details.

Whether the "boiling tower" is built with strong uniformly sized members such as Schamott stones, or better perhaps, in two alternate layers, whether the filling is clay, quartz or pumice stone, or similar material is not of importance.

There have been several adverse reports on the value of this denitration system in the technical literature, and a close scrutiny of the criticisms of the process as detailed by the critics are that much that is non-essential and superfluous may be removed and still obtain substantially as satisfactory results.

J. Rudeloff¹ points out that a number of nitroglycerol plants when equipped with the Evers system did not give satisfactory results, in the main attributable to unfamiliarity to the practical working details of the process, but as these details were recognized and their comparative significance allowed for, the technical difficulties were gradually solved. A water-while sulfuric acid of 60°-61.5° Bé., is readily obtained, practically free from nitrogen compounds and from iron, and in all characteristics commercially satisfactory sulfuric acid. Formerly with the older denitration processes, the same acid was almost black, carried from 0.3%-

1. Zts. Schiess. Spreng. 1907, **2**, 144; abst. C. A. 1907, **1**, 2636. See also Hall, Denitration of waste acid, E. P. Appl. 14529, 1915; abst. J. S. C. I. 1916, **35**, 64. E. Neumann, Sprengstoffe Waffen u. Munition, 1908-1909, **4**, 4, 14, 26, 42, 51, 62, 76, 88, 110, 136. V. Zelasko, D. R. P. Ann. Z-7426, 1911; abst. Kunst. 1912, **2**, 100; Chem. Ztg. 1912, **36**, 252. W. Poetsch, D. R. P. 29664. R. Schützphaus, U. S. P. 526752.

0.5% contamination of nitric acid, and seldom possessed a gravity exceeding 56° Bé., and was utilizable, therefore, only for the fertilizer industry.

Rudeloff points out that whereas denitrators usually have but one or two places for the introduction of air, Evers by superposition provides for four places both for the introduction of air and steam. While the providing of four places for the ingress of air and steam may be partially superfluous, yet on the other hand it is a certainty that a copious introduction of the hot acid and the height of the tower are prime essentials to the proper progress of the reaction. The main difficulty appears to be that in order to maintain the heavy and uniform flow of 60° Bé. acid, an unusually elaborate condensation system is necessary to completely condense the large bulk of nitric acid gases escaping.

Especial emphasis should be placed on the fact that when the hot air and steam enter at only two places, it is unwise to eliminate the partitions as described in the Evers tower. The reason for this is that the countercurrent flow of the gases and the acid is highly essential. It will be appreciated that there is a definite time factor necessary for each chemical reaction, and it must occur in the efflux of the acid at the proper height in the "boiling tower" when it is charged to a large capacity.

When completely filled with pumice, quartz or clay, it is possible that the efflux of acid, especially when highly contaminated with inorganic and organic impurities, will partially clog the filling, and form large and small irregular canals. These divert the flow of the acid and on that account materially impede the course of the reaction. As in the larger canals, much mixed acid and little of the purifying gases are brought into the requisite contact, while the condition is just reversed in the smaller ones. The entire course of the reaction under these conditions is irregular and unsatisfactory. On this account a high percentage of lower nitrogen oxides remain in the sulfuric acid, due to incomplete oxidation. The condensation is so closely related to the construction of the boiling tower, that it ordinarily does not receive proper attention in the de-nitration process. The so-called tourelles are used as condensing apparatus in the explosive industries, but have the two following objectionable features. Firstly, the condensation space is not completely utilized because

the gases travel with greater velocity from one outlet to the other without passing to the bottom. Secondly, the gases have a tendency to stratify and hence do not completely mix. The first objection may be partially overcome by extending to the bottom of the inlet to the tourelle, and the second one by filling the tourelle with coke or pumice.

The nest of tubes described by Evers and shown in the accompanying cuts are disadvantageous in that they are difficult to procure and expensive to install. Where it is desired to obtain an especially pure nitric acid, the mixing and continuous re-mixing of the gases is of paramount importance. From the above procedure, it is self-evident that the fluid or semi-fluid and solid substances must be intimately intermingled. Naturally the system must be long enough and of sufficient capacity to assure the complete condensation of the gases under most active ebullition, and the last condensing towers are useful only for the spray and gasified products.

After prolonging the concentration and recovering the remaining nitric acid, after a short time a pale yellow nitric acid of about 40° usually is obtained in the proportion of about 80%. Where the conversion of the nitric acid in the upper part of the boiling tower is carried out in such a manner that the nitric acid collects and enters undecomposed, from the boiling tower into the condensation system, then the condensation of the gases is uniform, and they are mixed and cooled so that the remaining nitrogen oxides are not condensed in the tube system. It should be appreciated that the so-called nest of tubes are the only means for sufficiently mixing and condensing the nitric acid gases. In those instances where the spent acid contains much organic impurity, which has not been oxidized to CO_2 in the boiling tower, but is readily sublimed in the condensation system (nitrobenzol or nitrotoluol spent acid), in such instances these nests which work so efficiently with the spent acids from nitrocellulose and nitroglycerol manufacture, cannot be used at all because they clog up too readily, and would check the draft in the condensation system.

In such cases, the so-called cellarious vessels have proven satisfactory. When used in rows of three, they are immersed in casks of cold running water, and directly connected in back of the

boiling tower. By this arrangement the impurities carried over from the boiling tower (such as di- and trinitrotoluol compounds) condense or immediately sublime in the cellarious vessels and where it can be melted and extracted from time to time, by heating the water in the cooling casks.

Clay towers with coke filling are considered most satisfactory, but it must be uniformly screened. It is also advisable to have hollow divisions in the several layers of coke, similar to those described in the boiling tower filling. The improvements in denitration as evolved and perfected by Evers as a whole, may be considered as basic, the economy in coal and labor being very apparent.

The apparatus when properly installed is semi-automatic, necessitates no special supervision, the denitrator injectors requiring no particular attention, while the acid circulation is maintained by means of automatic pressure vessels. One workman is said to be sufficient for the manual labor of an entire installation.

One installation in a twelve-hour day will handle 8000-10,000 k. waste acid of the usual composition (say 70% sulfuric acid, 10% nitric acid and the balance water), the sulfuric acid being eventually recovered colorless and without loss while the loss of the nitric acid is alleged to be only about 0.1%.

Based on a waste acid of the average composition of 74% sulfuric, 8% nitric, and 18% water, with 10,000 kilos denitrated in a ten-hour day, the following figures are submitted as representing an average factory run, and one that could be indefinitely duplicated.

(1) The sulfuric acid is recovered perfectly clear, free from nitrogen compounds, and with a loss of 0.08%.

(2) The recovered nitric acid varied in density from 36°-40° Bé., containing traces only of sulfuric acid and a maximum of 0.3 % nitrous acid. Maximum loss 0.2%.

(3) Coal consumption 3% based on the weight of the waste acid treated.

(4) Coke consumption 1.6% based on waste acid treated.

(5) Repairs and upkeep small. Labor, one man.

The V. Vender Denitration System. This invention¹ is based on the alleged discovery that hot gases generated by the combustion of the nitrogen of the air by an electric arc, by direct contact denitrate nitrosulfuric acids recovered after nitration treatments (as in the nitration of cellulose, glycerol and aromatic compounds) in a much more efficient manner than is accomplished by means of heated air, and that by the use of these gases it is possible to obtain sulfuric acid of 98% strength which is perfectly clear.

Such results must be attributed to nitric oxide contained in the gases obtained by the combustion of the air, and is said to be accompanied by another advantageous result, in that the synthetic nitrogen oxide can be more easily condensed, for nitrous and nitric acids of the recovered acids, oxidize it, and the gases obtained are therefore richer, as all the nitrogen oxides are present in a form easy to condense.

The process is commercially carried out by means of a system of two towers arranged relative to each other in such a manner that the hot gases produced by the combustion of the air heat the first tower outside, and then pass into the interior of the second. The second tower (the denitrating member) is fed with the recovered acid which it is desired to denitrate, while the hot gases above mentioned, travel in it in an upward direction. At the bottom portion of the tower, concentrated sulfuric acid is withdrawn, and at the top are disengaged the nitrous acid gases which, upon being introduced into an ordinary condensing apparatus, give nitric acid of about 60%. The first tower containing the distilling apparatus is fed at the top with nitric acid of 60%, and with a portion of the concentrated sulfuric acid coming from the second tower; from this mixture is distilled nitric acid which is liquified by condensation in an ordinary condensing apparatus, to 98%, while at the bottom portion of this tower sulfuric acid of about 75% is withdrawn, which is sent direct to the second tower.

In this manner, according to the patentee, the whole of the

1. E. P. 18280, 1909; abst. J. S. C. I. 1910, **29**, 696. F. P. 405319, 1909; abst. J. S. C. I. 1909, **28**, 423; C. A. 1911, **5**, 1665; 1918, **12**, 631; Mon. Sci. 1910, **73**, 172. Belg. P. 218232, 1909. Aust. P. 43749, 1910. Swiss P. 48469, 1909. See G. Kynoch & Co. and A. Cocking, E. P. 27718, 1896.

sulfuric and nitric acids present in the original waste acid is obtained at a degree of concentration up to 98%.

Irrespective of the type of denitration system employed, the recovered acids are either passed through one of the well known concentration processes for further use in nitration or the acid is sold separately as such.

The efficiency of a denitration plant is usually determined by an examination of the exit gases, the efficiency of the installation being directly comparable with the minimum of escaping nitrogen fumes, as determined by aspiration of the escaping fumes into water and determination of the acid by titration.

According to G. Patterson¹ the revivification and denitration of nitrating acid may be most advantageously carried out in cylindrical iron vessels with pipes for running in and off of the acid. The mixing and moving of the acid is done by compressed air. The air enters from pipes placed at the bottom of the tanks and provided with a number of holes, from which the air escapes and which are closed at the end. Such a container is 21.5 m. long and possesses a diameter of 4.6 m. and holds about 19,000 kg. acid, one of 32 m. length and 5.5 m. diameter about 41,000 kg. Each container is provided with an air vent, which is closed with a wooden plug if pressure is to be applied. The containers are placed in batteries. Two large containers are used for storing and holding the spent acid, 8 smaller ones for the acid to be added for reinforcing, this acid consisting of nitric acid and H_2SO_4 of 98%. A small container is placed on a scale and connected with a 14 m. long pipe with another container. The spent acid is collected in one of the large containers until it consists of about 38,000–40,000 kg., mixed by blowing air through for an hour, a sample taken and carefully analyzed. The amount of reinforcing acid is calculated according to the analytical result, 15,000 kg. of the spent acid drawn in one of the containers standing on the scale, the requisite acids added and well mixed with compressed air. The whole charge is now united in another large container and well mixed again by blowing air through for 1 to 1½ hours. A spent acid apparently may be revivified an unlimited number of times, provided that the content of nitrous

1. Eighth Intern. Cong. Appl. Chem. 1912.

oxides does not exceed 5.5%; this however, only in the case of the English method, where such a large excess of acid is used.

The spent acid is denitrated for the recovery of the sulfuric acid and nitric acid. The average composition of the spent or waste acid in the nitrocellulose manufacture is usually 70% H_2SO_4 , 10% HNO_3 and 20% H_2O .

Guttman Nitric Acid Denitrating System.¹ In 1896, O. Guttman departed from the methods hitherto used where the reaction between the gases and liquids had been effected mostly by means of pipes and towers in which the gases passed upwards and the liquids downwards being intercepted in towers filled with material unaffected by the acid vapors, the obstructions being so arranged as to allow a certain quantity of liquid to accumulate and thereby concentrate before any ran through. His original process consisted primarily in filling the towers with "denitrating stones" as shown in Fig. 127 combined with a system of water-cooled tubes, condensing towers and suitable vessels for the reception of the recovered acids.

For inducing a current of the oxides of nitrogen exhaust fans were provided, and for the transportation of the acids, automatic compressed-air elevators were installed.⁶ At the top of the denitrating stones an arrangement for spraying the waste acid was provided, together with an earthenware exhaust pipe for the withdrawal of the nitric acid vapor, an overflow arrangement for the withdrawal of the sulfuric acid being provided in the lower part.

As the nitric acid evaporates from the heated waste acids and collects in an exhaust pipe in the form of nitrous vapor, the sulfuric acid collects in the lower portion of the denitrating tower through an overflow into especial vessels, artificially cooled. The sulfuric acid thus obtained varies from 35°–55° Bé. in strength and is opalescent and dark colored from organic impurities contained therein. In this condition it is utilizable for the manufacture of superphosphates and other artificial manures.

The nitrous vapors issuing from the towers packed with denitrating stones are conducted through earthenware pipes with forced draught, through a cooling system and into storage recep-

1. See Chem. Trade J., 1915, 56, 211. J. S. C. I. 1901, 20, 7.

tacles. An air-cooled unit is also incorporated with this system so that the nitric acid condensed in the apparatus runs also into this vessel. Any uncondensed vapors next pass on to a system of four towers connected in series filled with hollow vitreous members, the arrangement being so that the gases pass in a direction contrary to a liquid capable of absorbing them. Each tower of the series is provided with an automatic pressure vessel, which passes any acid collected therein on to the next tower. The nitric

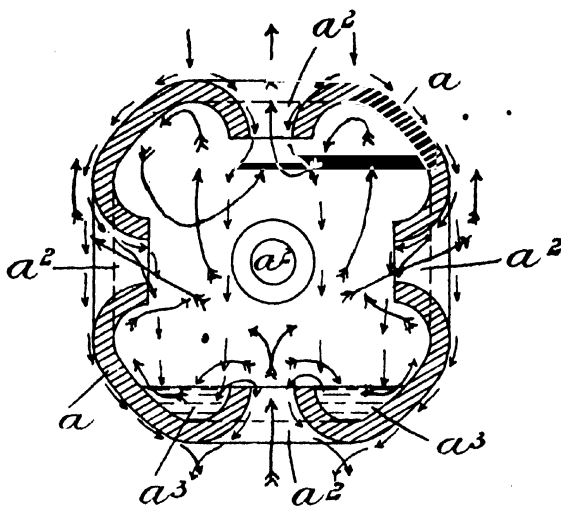


FIG. 127.—GUTTMANN DENITRATING STONES

acid collected from these towers is of 30°–42° Bé. strength. The exhaust from the last tower of the series is connected to the chimney.

- The Guttman system for converting into nitric acid the nitric peroxide resulting either from the denitration of waste acids or in the manufacture of nitro-compounds, is shown in Fig. 128. In this apparatus *A* is the denitration portion of the usual kind from which the nitrogen oxide gases issue through a pipe *a* and into an earthenware receiver *B*, which is filled with coke,

broken glass or balls,¹ and tends to minimize breakage of the apparatus through the gases being too hot. The gases are then withdrawn by an air ejector *C* and forced to two or more vertical towers or series of pipes *D*, also filled with coke, down which a fine stream of water trickles. The unabsorbed gases pass through a tube *F* into a condensing apparatus *G*, while the liquid flows into a distributing tank *E* which directs small streams to the top of each bend of the condenser, and also to the receiver *B*. Any gases still unabsorbed pass upwards through a pipe *r* to a coke tower *H*, down which a small stream of water flows. The nitric acid flows from the condensing apparatus *G* to the collecting vessel *L*, from which it can be drawn off at *p*.

By this process it is claimed the acid will not only be of the maximum strength but also that the current of the acid gases is suitably retarded with the result that the gases are entirely converted into nitric acid.

The denitration process as described by C. Jahn² and the Sprengstoff A. G.

Carbonit³ is intended primarily for the denitration of those waste acids formed as the result of the nitration of aromatic bodies, which bodies are present in the waste acids in solution or suspension, or both, and when so present have a tendency to clogging of the condensing plant used in the recovery of the nitric acid. These substances (nitrobenzol, nitrotoluol, nitro-cresol) which are liquid when heated, are prone to deposit on the

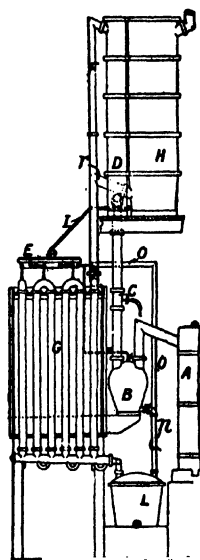


FIG. 128.—GUTTMAN SYSTEM

1. E. P. 14774, 1896; 18189, 1897; 13694, 1901; abst. J. S. C. I. 1901, 20, 587. D. R. P. 136678; abst. Mon. Sci. 1903, 59, 71; Chem. Centr. 1902, 73, II, 1349; Chem. Ztg. 1902, 27, 1207; Chem. Zts. 1903, 2, 276, 282; Jahr. Chem. 1902, 55, 343; Wag. Jahr. 1902, 48, I, 351; Zts. ang. Chem. 1902, 15, 1249.
2. U. S. P. 1149585, 1915; abst. C. A. 1915, 9, 2710; J. S. C. I. 1915, 34, 960.
3. E. P. 11854, 1913; abst. J. S. C. I. 1913, 32, 1130; C. A. 1914, 8, 2807; Chem. Ztg. Rep. 1914, 38, 299.

walls and adhere to the interior of the condensation towers, so that in a short period of time the denitration is interrupted until the stoppage is removed.

The patentee claims that these drawbacks are overcome by performing the denitration operation in the apparatus shown in Fig. 129. Referring to the drawing, it is intended to be understood that the gases arising from the boiling drum pass as usual first into a preliminary retort, and then into a conduit 1, which

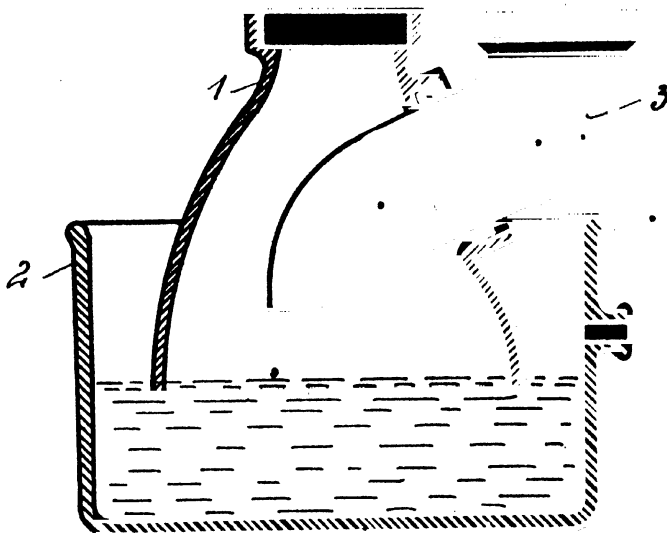


FIG. 129.—THE JAHN NITRATION PROCESS

is open at its lower end and dips into a vessel 2 containing water or dilute nitric acid. The conduit 1 is funnel shape and receives a discharge connection 3, which latter does not dip into the water or dilute nitric acid.

In order to operate the apparatus, the organic bodies which have been sublimed or carried along by the nitric acid gases cool off along the walls of the conduit and impinge on the surface of the water where they are solidified, while the gases pass through the discharge outlet. The water or dilute nitric acid becomes

enriched with nitric acid, and is then discharged at a strength of 36° Bé. through an overflow. The solidified organic bodies settle at the bottom of the vessel and along the walls and, as the latter is open, can be easily removed and recovered. The nitric acid gases pass through a second, and, if necessary, a third conduit, with a separating appliance, and are finally completely absorbed in a condensation plant, such as a coke tower.

Recovery of Nitrous Fumes as Nitric Acid. In nearly every nitration operation, especially when conducted at comparatively elevated temperatures as in the centrifugal nitration of cellulose, there is a considerable evolution of nitrogen oxide fumes owing to the heat of the reaction and the unavoidable decomposition of nitric acid which such operations necessarily entail. Where manufacture is sufficiently extensive to warrant the installation, these gases consisting primarily of NO, N_2O_3 and N_2O_4 with smaller amounts of anhydride (N_2O_5) can be condensed and economically converted into nitric acid.

In one arrangement which has proven satisfactory on a commercial scale, exhaust fans are connected to the individual nitrators, from which the fumes are drawn through an exhaust pipe, usually arranged so that the several exhaust pipes converge into a common main, the area of the latter being preferably greater than the sum total of the areas of the individual pipes, and which leads to a tower or series of towers where the oxidation of the nitrogen oxides to nitric acid takes place. The arrangement of this tower depends as to whether the main object is to recover and condense the maximum of fumes or merely to render them as innocuous as possible before their discharge into the atmosphere. Ample provision in cooling and condensing surface should be provided, as the reaction requires considerable time. If the idea in mind is merely to render the gases harmless, they are caused to pass through a multiplicity of large wide towers and in a circuitous direction before discharge into the atmosphere. In a centrifugal nitrator of the Selwig and Lange type, it is advisable to provide at least 8-10 cubic meters of tower space for effective working, and if nitration is carried on at high temperatures, this cubical contents per nitrator should be regarded as a minimum.

The entire tower battery may economically be divided into a larger unit in the front and a smaller one directly behind, the

air circulation being so arranged that it diminishes in speed and intensity from the larger to the smaller. The rear battery is charged with an amount of acid which is passed to the front battery in such quantity and constancy as is required to induce the maximum concentration. Regeneration systems are capable of producing an acid up to 36° Bé. in strength, with a small upkeep, and with a labor cost that is very low.

In one method the nitrous fumes first pass through an air cooler, thence through two series of towers filled with hollow balls, the circulation being maintained by means of an earthenware exhaust fan connected to the rear tower. The extent of the pre-cooling will depend upon the temperature of the entering nitrous gases. The gases usually pass from the pre-cooler to the underpart of the first tower and after passing through it are piped from the top of the first tower to the bottom of the second tower, and the cycle there repeated.

A point of paramount importance in the regeneration of these fumes is the imperative necessity of reducing the liquids to the finest state of subdivision, that the intermingling may be as thorough as possible. This is best realized by the interposition of an exhaust fan or by means of vitreous or earthenware disintegrators. Such an apparatus when operating with a maximum efficiency results in the atomization of the liquid, and by thus insuring intimate contact the maximum of efficiency is attained.

Nitric Acid Recovery by Solvents. The Dynamit Akt. Ges. have disclosed a process for the regeneration of nitrogen oxides which depends upon the solution of these fumes in esters of the paraffin alcohols, ethyl, propyl, butyl and amyl formates, acetates, propionates and valerianates being especially applicable. They propose to absorb the nitrous fumes in these organic liquids, subsequently expelling the nitrogen compounds by distillation at temperatures below the boiling point of the aliphatic ester. Amyl acetate appears to have the maximum solvent power, one part of which, at ordinary room temperature, being capable of dissolving or absorbing nearly 20% of its weight of N_2O_3 and NO_2 , which is considerably in excess of any other liquids which have heretofore been proposed for this purpose. The nitrous fumes are easily recoverable from such solutions by passing air or inert gas through

the ester when the latter is heated below its boiling point.

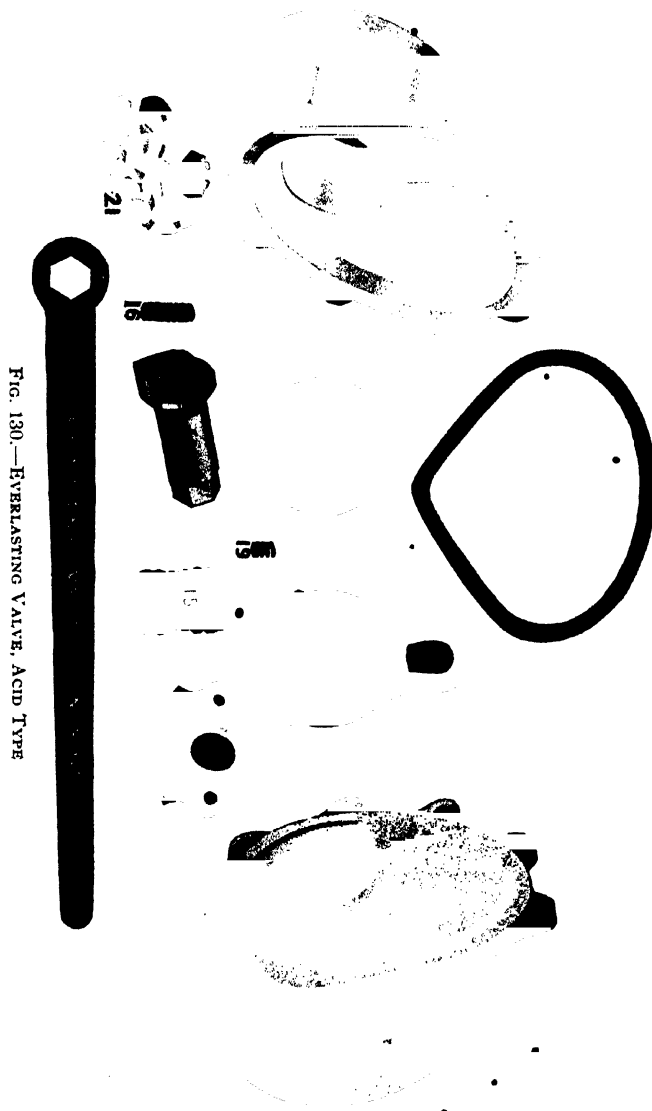
Those esters which are comparatively insoluble in water (amyl acetate, amyl propionate and amyl valerianate) when saturated with the nitrogen oxides, may have the latter almost completely removed by the addition of water, thus converting the nitrogen into nitrous and nitric acids, which may be separated mechanically from the mixture, the water and ester forming an immiscible layer from which the aqueous acid may be withdrawn from the bottom layer, the line of separation between the acid and ester being clear-cut and distinct.

Acid Valves. An exceedingly important topic in connection with the question of mixed nitrating acids—and one which is of considerable financial importance—is the subject of acid valves. In the installation of a ten wringer nitrating unit with the acid supply and waste acid in connection therewith, over one hundred valves are required in a modern installation. Of the various types of acid valves used for this purpose in the United States at the present time, the Everlasting Valve has been most extensively employed¹ and widely used. The general arrangement of the working parts of this valve is illustrated in Fig. 130, and assembled in Figs. 131 and 132. The working parts of these valves do not wedge, being independent, "floating" parts, the disc always sliding in contact with the seat, and with a rotating movement which regrinds the faces of both.

When full open the valve is merely a portion of the acid pipe, so that the joints between the two bonnets may be broken, thus leaving all the working parts easy of access. The bottom bonnet and disc may be refaced without special tools, spare parts are obtainable, and this prolongs the period of efficient surface. The nitrating valves are of high silicon gray cast iron, machine ground. In the "screwed" acid type Everlasting valve shown in Fig. 131, and known as a "quarter-turn" valve, the lever is always installed on the far side from the pressure, being easily removed, as is the stuffing box gland, to permit of repacking of the post.

The "flanged" acid type valve (Fig. 132), while increasing the number of packed joints due to the use of the flanged connection, is nevertheless desirable where the size of the valve exceeds

1. Manufactured by the Everlasting Valve Co., of 2 Rector St., New York City, and developed under the direction of John H. Allen, President of the Company.



2". Inasmuch as a valve must be regarded as a part of the working equipment, it should be so installed as to be easily removed from the line if desired.

In the "double disc" of acid type valve (see Fig. 133), which is made both screwed or flanged where the valve may be subjected to pressure from alternating directions, its field of usefulness is

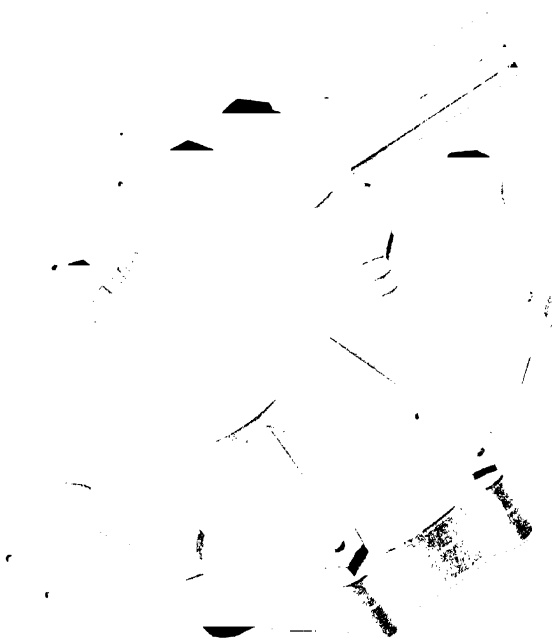


FIG. 131.—EVERLASTING VALVE, ACID TYPE, SCREWED

mainly for acid storage tanks, as indicated in Fig. 135, this photograph being taken from the installation of the Nixon Nitration Works at Metuchen, N. J.

In the type of valve illustrated in Figs. 134 and 136, and designed primarily for use in connection with the du Pont or Mechanical system of cotton nitration (see Chap. X), the mixed acid is brought to the measuring or weighing room on the top floor through

either a $1\frac{1}{2}$ " or 3" line under air pressure, and enters the measuring tank through a 3" Everlasting acid type valve with shield (Fig. 134). This valve is built with a stub lever which comes directly in front of the broad eyelet in the shield, *only* when the valve is closed, the valve being functioned by means of a socket wrench, the large head carrying the socket, closely fitting the eye in the shield.

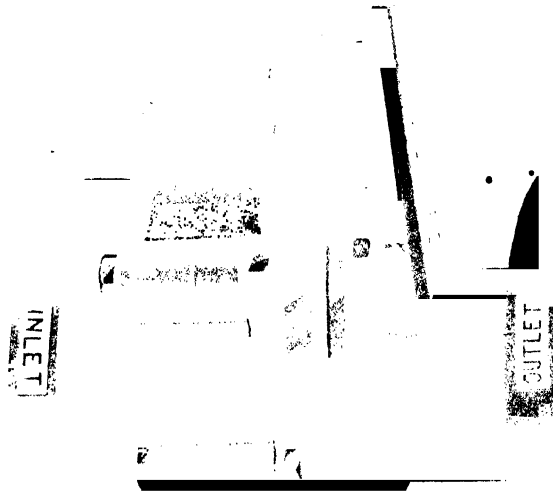


FIG. 132.—EVERLASTING VALVE, ACID TYPE, FLANGED

Whenever the operator moves the wrench to open the valve, the wrench engages in the slot and is not removed until the proper amount of acid has been run in the tank as indicated by the gauge. The measuring extends from the tank through a 3" discharge line over to another 3" valve, which branches into four distributing lines, each of which is likewise controlled by a valve of the type shown in Fig. 134. The operator possesses only one socket wrench for the five valves in his unit. He first carries the

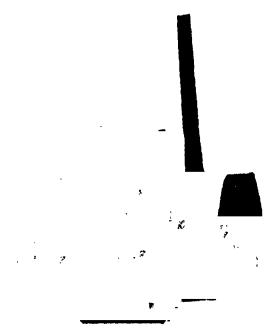


FIG. 133.--EVERLASTING VALVE,
ACID TYPE, DOUBLE DISC

wrench from the intake valve on the measuring tank to one of the discharge valves, opens the latter, and remains there until the line is drained, for he cannot remove this socket wrench without closing the valve. When this line is drained the operator removes the socket wrench, returns to the measuring tank, and the operation is repeated.

In the meantime the cotton has been weighed and conveyed to the nitrating pot located on the floor directly underneath. At the close

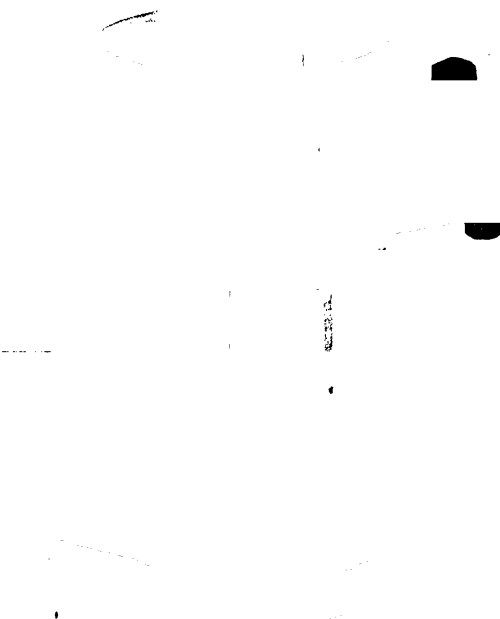


FIG. 134.--EVERLASTING VALVE, ACID TYPE, WITH SHIELD

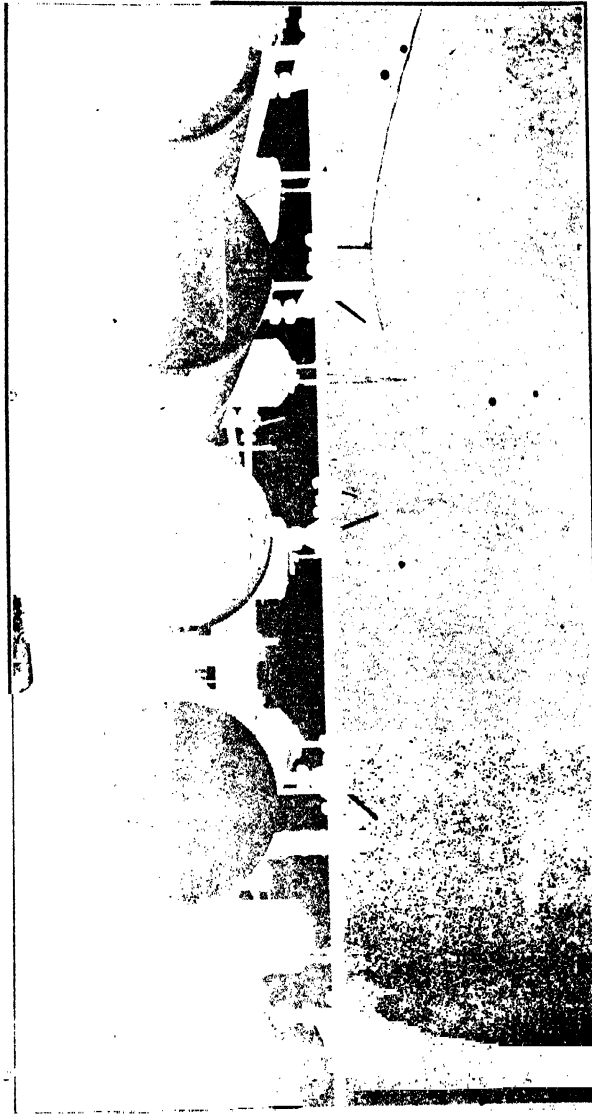


FIG. 135.—Mixed Nitrating Acid Tanks, Showing Installation of Acid Valves •

of the nitration period the valve shown in Fig. 136, and known as the acid type extension handle form, is opened, and the nitrated mass together with the spent acid is discharged into the basket of a centrifugal. There are four of these nitrating pots and discharge valves (6" size) per unit. A flexible nozzle may be swung from each of the four discharge lines so as to convey the contents of the nitrating pot into a common centrifugal.



FIG. 136.—EVERLASTING VALVE, ACID FORM, WITH EXTENSION HANDLE

Manufacture of Nitrocotton Mixed Acid, English Practice.
The following details of acid mixing for nitrocellulose manufacture show the thoroughness and thoughtfulness for seemingly unimportant points, indicative of English chemical practice in general.

Preliminary Mixer. A mixer which has given general satis-

fraction is a cylindrical vessel of three-eighths inch boiler plates riveted together to form a tank 5' high and 10' diameter, flanged at the top to take a cover. The latter is bolted together in four equal sections, the whole being bolted against asbestos packing to the flange of the mixer. Through a center casting carrying an oil seal fitting, is suspended the stirrer of 2½" shaft, the propeller of which revolves at a height of 16" from the bottom of the mixer, inside a cylinder of half-inch plate, open at each end, this latter being mounted on four legs 10" long, being 28" high over all. Symmetrically placed around this, i. e., one under each lid sector, are four drawn mild steel coils standing on acid-proof bricks (3") for water cooling purposes. Through suitable holes in the lid are fitted:

1. A manhole with lid.
2. A 2" mild steel pipe dipping 4' to deliver oleum, this pipe being connected with 3" mains leading direct to Mannheim and Grillo oleum storage tanks.
3. An exactly similar 2" line for sulfuric acid (for doping purposes) feeds from the mixers spent acid storage.
4. A 3" line feeding concentrated nitric acid from the retorts (or stills), and which dips to within a foot of the bottom.
5. A 3" earthenware line feeding weak nitric acid from the weak nitric acid receivers of all producing plants, and provided with 3' 6" earthenware dip pipe.
6. A 4" earthenware fume line leading to absorption towers for the exhaustion of fumes evolved in mixing.
7. A 4½" inspection hole for sampling, covered with a lead lid.
8. A 1" hole carrying a 40" thermometer suspended in the center of one of the four coils.
9. A ¼" dip hole left open for dip rod.
10. A ¾" rod carrying a regulus metal plunger seated to exit casting.

In the above apparatus all acid flows to the mixer by gravity through the respective lines.

The exit is preferably a cast steel swan neck having the seating against the bottom of the tank carrying the above plunger. This swan neck leads directly to a Quinan valve, and then a cast iron plug cock, and so to the pumps via 3" mild steel lines. The

mixer stands on a base of acid-proof brick work and channel iron, 18" high. A lead mixer is exactly similar except being lead lined, and is occasionally used for fortifying with sulfuric acid and waste nitrating acid in conjunction with nitrocotton mixed acid.

In addition, each mixer is provided with a gauge glass, the fitting for which is tapped to the boiler plate 4" from the bottom, the glass being clamped in a vertical position over a carefully graduated lead scale. The coils are drawn mild steel of $1\frac{1}{2}$ "- $1\frac{3}{4}$ " internal diameter and walls $\frac{1}{4}$ " thick, having 13 turns supported at equal distances by four iron standards bolted symmetrically. The cooling surface is 9750 sq. in. with a total length of 135' 6", and stand 4" high. The diameter is 3", with the inlet and outlet protruding through the lid of the mixer, leaving screens and socket for connection to the water main.

Experience has demonstrated that best results are obtained when these coils are jacketed where the inlet and outlet arms protrude through the lid. This prevents fumes—which give rise to weak acid—corroding the coil. Coils which have given out at the welds are repaired by re-welding the jacketing, in both cases mild steel jackets being welded to the coil.

The stirrer is suspended, and attached to the mixing house girder by bracket bearings, the actual suspension being from Hofmann ball bearings. The shaft is $2\frac{1}{2}$ " diameter steel, carrying a propeller with 8" blades, and is belt driven (the belt pulley being 4" wide and 27" diameter), from a live shafting and clutch pulley driven by a 10 h. p. Siemens motor, the belt being cross drive turned through an angle of 90°. On revolving the stirrer (160 r. p. m.) the acid is drawn up inside the drum to meet a disrupter clamped to the shaft 6" above the top of the drum. This quickly and efficiently mixes the acid.

The *Mixing House* is preferably constructed of corrugated iron over steel girders, about 15' high and standing on an acid-proof brick mat set with bitumastic Nori cement on ferro concrete foundation. It is surrounded by a deep split pipe gutter of earthenware, so that washing down by flushing for cleanliness is comparatively easy. The mixer house should be well ventilated, and is only closed in for about one-third of the length to give shelter to the pumps, motors and operatives. This part is steam heated in cold weather. The wall of the house is provided with

brackets to carry the above mentioned line shaft running the whole length of the house on one side, and about 9 feet from the floor.

• The *Revivifying Acid Blenders* are cylindrical tanks of five-eighths inch boiler plate, double riveted together in sections 20' in diameter and 12' deep, and having a dome-shaped lid. Each blender is provided with stirring arrangement, but carries no coils. The stirrer is similar to that used in the mixers, but is suspended from a bracket built to the center casting of the lid. It is a vertical shaft carrying a propeller at a height of about 30" from the bottom of the tank. The propeller is surrounded by a drum which is about 6' in height from the bottom of the blender, and supported on four legs. About 6" above the top of the drum is the disrupter as in the mixer, the disrupter being a flat strip of iron 3" wide and 18" long, clamped to the shaft at its middle. The lids have each a man-hole casting and lid, a 4" mild steel fume line, and a sample hole fitted with a lead tray through which a dip rod may be lowered from a pulley in the roof of the blend house. The inlets to (say) Blend 1 are: (a) a 3" mild steel line, boxed and steam heated, feeding oleum by gravity from the oleum storage; (b) a similar line feeding sulfuric acid by gravity from the sulfuric acid storage; (c) a similar line feeding nitro-cotton mixed acid.

The blender stirring apparatus is driven by a 5 h. p. motor, placed on a platform at the edge of the blender, power being transmitted by a 4" belt. The blender stands 3' from the floor on brickwork and channel irons. The floor is preferably of acid proof brick, and the area should be adequately drained. It is not necessary to enclose the blenders, but the stirring pulley and driving motor and belt should be protected from the weather, being enclosed in wooden casings. The only entry is from the revivifying acid mixers, the latter being connected by a 4" mild steel line, distributing by 3" mild steel line to each tank. Delivery is by a cast steel 3" swan neck with usual fittings, and check valves, and delivers to the nitrocotton mixed acid blenders. They are fitted with 4" earthenware fume lines.

• The *Nitrocellulose Mixed Acid Blending Tanks* are 20' x 12', of the same specifications as the revivifying acid blenders, being

equipped with stirrers. Each blending tank has the following inlets:

1. A 3" mild steel line for sulfuric acid leading from the vitriol storage.
2. A similar line leading for rejuvenating acid, leading from the fortifying acid tanks.
3. A 4" main of mild steel, feeding spent acid from the nitro-cotton spent acid storage.

Each blending tank delivers to a layout of several pumps (usually 6), which in turn run to the nitrocotton mixed acid storage tanks, and each is fitted with a 4" earthenware fume line.

The Blend House is usually constructed of wood, and contains the blending tanks, with an offset for the pumps and their connections. From the roof are suspended the dip rods on pulleys. The entire building should be well ventilated and provided with suitable gantries and protection railings.

Nitrocotton Mixed Acid Storage Tanks are similar to the blenders, being 20' x 12', of $\frac{5}{8}$ " boiler plate, and not equipped with stirrers, being unlined. Each tank is provided with an inlet pipe, a 3" lead from the blend house pumps and one delivery, the usual 3" swan neck and plunger fittings leading via a Quinan valve, and a 3" cast iron plug cock to the nitrating house. The domed lid is fitted with a center casting carrying a tripod for the suspended dip rod over a $1\frac{1}{4}$ " dip hole. All are mounted on brick piers to a height of about 20' above the ferro concrete mat on which the tanks are built, the run-off being by gravity.

Nitrocotton Spent Acid Tanks are similar to the mixed acid storage tanks previously described, those into which the nitro-cotton spent acid is pumped, being lead lined. Each tank is provided with two 3" inlets, one being of lead and the other of mild steel, which latter is the pump line leading from the spent acid wells from which the spent acid is run off after nitrating. The deliveries are in each instance the usual 3" goose neck, and by duplicating and interchange lines the acid from any two tanks may be run down together to any mixed acid blender by gravity. Also leading from these acid interchanging lines is a 3" pipe leading to the spent acid pumps situated on the ground level, the tanks being elevated about 22' on brick piers. These pumps are designed for the delivery of a certain percentage of the total spent acid to the stills for distillation (usually 30%–40%); in conjunc-

tion with these pumps and also with the blend house pumps, is an acid egg of about 25 tons capacity for blowing acid in an emergency. It is seldom used except as an acid pump and for draining various mixed acid lines. The spent tanks are located in the open—the same as the storage and fortifying acid tanks—and are preferably placed between the two batteries of storage tanks, the whole layout being arranged symmetrically about a line through the spent acid and blender tanks.

Capacities. So far as standard sizes and differentiation in calibration are concerned, corrections obtained by absolute weights of water to account for the presence of a stirrer or a lead lining are applied for all dissimilar acids used in the various tanks. On the nitrocotton mixing system the *approximate* capacities are, for: mixer, 18 long tons; fortifying acid, 175; mixed acid, 180; blender tank, 180; spent acid tank, 175; and acid egg, 25 long tons.

Manipulation of the Process. Assume that the object is to produce nitrocotton mixed acid of the composition H_2SO_4 , 61.7 ± 0.3 , HNO_3 , 23.7 ± 0.3 , H_2O , 14.6 ± 0.1 , the operation is carried out by fortifying a certain percentage of nitrocotton mixed acid returned from the nitrating house (usually 60%-70%) with fortifying acid, the first essential, therefore, being the

Production of Revivifying Acid. In general it has been found that the composition of the fortifying acid varies within 2% or 3% of its composition according to the acid balance over the section which determines the weekly program, and hence the composition of the fortifying acid for that week is dependent upon the percentage of spent acid to be pumped to the stills. Naturally the more spent acid returned to the stills, the greater the dilution of the fortifying acid in a given tonnage of nitrocotton mixed acid. If the average composition of the fortifying acid is considered to be: H_2SO_4 , 60%; HNO_3 , 33%; H_2O , 7%, we have available 20% oleum (104.5% H_2SO_4), 92% sulfuric acid, 90% nitric acid, a little nitric acid from the stills, and a little 92% nitric acid from the retorts. Knowing the weight of the total desired mixture, the percentage of each constituent is calculated as stated elsewhere herein, and from this the unconfirmed (by analysis) mix is produced. The stock inventory of the various acids concerned will determine what combination it is feasible to employ to obtain the percentage composition desired. In mixing but little heat is

developed except when oleum is used, and as previously mentioned, this is reduced by residual mixing. The acids are run into the mixer always in the following order: oleum, by careful dipping; sulfuric acid, ditto; strong nitric acid, and also weak nitric acid, by careful dipping at the producing plant receivers. All the above are calibrated and the strength of each acid first determined by laboratory analysis. When all acids have been run in, and cooling has brought the temperature to about 25°, the mixture is pumped to the desired storage tank. From here it is pumped to the blender, where it undergoes a two-hour agitation, sampled, and if within the allowable fluctuating range of composition, is placed in the finished acid storage system. The mixing, stirring, sampling and analysis requires a nine-hour cycle.

Transfer and Distribution of Concentrated Sulfuric Acid. In connection with the preparation of mixed nitrating acid, is the series of operations of the handling of the sulfuric acid portion of the mixture. Concentrated (92%) sulfuric acid is delivered from the Gaillard concentration plant into (preferably) two series of lead storage tanks, five being allocated to each Gaillard house. As soon as the acid has been delivered to these storage tanks it may with propriety be considered as belonging to the mixers whose function it is to pump it away to the consuming plants according to their requirements as indicated by the general acids program. In a self-contained nitrating unit, the consuming plants are: (a) the Grillo oleum plant; (b) the nitric retorts; and (c) the acid mixing system.

Each Gaillard house, therefore, should be arranged in such a manner that the respective storage tanks lead into a common mild steel line via a plunger outlet and a 3" cast iron plug cock. From this common line there may be three leads, two to acid pumps, and a third to a 25-50 ton acid egg used in an emergency in conjunction with or instead of the pumps. These pumps preferably each deliver to a Y-piece controlled by a cast iron plug cock, one lead feeding the Grillo and the other the nitric acid retorts and the acid mixers storage. The lines from both houses should converge into a common line outside the plant.

Sulfuric Acid Storage. At the Grillo this may consist of a suitable number of standard 30' x 9' storage boilers, each of capacity of about 90 long tons 92% H_2SO_4 . At the nitric acid

retorts, in conjunction with the retort houses are provided one or more storage boilers of about 75 tons capacity, and arranged with dip rod and tripods as previously described. Of these, one is reserved for mixer stock, the balance having common delivery lines to the retorts vitriol feed tanks. All the above storages are best fed and delivered by 3" mild steel pipes, the deliveries being controlled by the usual cast iron gland plug cocks and stop valves, and all are built on brick piers so that gravity delivery is provided for all the plants.

Distribution of Condensed Sulfuric Acid from Storage Boilers. The two ton feed tanks in connection with each nitric acid retort are individually filled to a definite dip. The foreman in charge of the various storages keeps a storage tank turned on to the mixers at the mixing houses and to the nitrocotton blending.

Those unforeseen emergencies which inevitably arise, and usually when least expected, apparently are taken into consideration in the above described acid storage and circulation scheme, it being borne in mind that the success of the transfer and distribution depends primarily upon the accurate measurement of all tanks before and after pumping so as to be in a position to decide precisely the amount to be pumped, and especially to guard against spills from over-pumping. Reliable and conscientious men are required for this work as with the mixing process itself.

Water. The chief use of water is for the cooling coils of the mixers. For this purpose a 4" water main should run the length of each mixing house. From this main is provided a 2" lead to each mixer, and having opposite each coil a further 1½" lead, supplying the inlet to each of four coils. Each 2" lead is controlled by a 2" water sluice valve cutting off entire water supply to the house. A ¾" water main encircles the mixers at a height of 4' 6", being by-passed and controlled from the 1½" main. This line is perforated with ⅛" holes on the inside, and can be used to cool the mixes by external spraying in cases of emergency, generally when all coils have to be closed due to a burst coil. The other sections of the plant are fed by 2" mains with inch leads to bib cocks with screw fittings for 1" water hose for washing down.

Air. But little air is used excepting in an emergency for

blowing the acid eggs already mentioned. The feed to these eggs is by a 1" line fitted with a pressure gauge and 40–60 lbs. pressure being always ample for all blowing purposes. In addition a small $\frac{1}{4}$ " air jet reduced to 10 lbs. per square inch inserted in the absorption tower should be provided, as also one for air agitation fitted to the nitrocotton spent acid tanks—rarely used.

Mild Steel Pipe Lines. Lines for all mixed acid and concentrated sulfuric acid and oleum should be of mild steel, being to the Association Standards of steam fittings. All pumping and drawing mains are 3" with the following exceptions:

(a) Delivery main and header from the mixed acid blend house to the storage tanks.

(b) Delivery lines from the spent tanks to the nitrocotton acid blenders.

All these should be of 4" mild steel lines while the feed lines for oleum and sulfuric acid to the mixers and to the 2" Douglas pumps at the weigh tanks are 2" mild steel lines.

All lines containing oleum are steam heated by $\frac{1}{2}$ " lagging lines and whole boxed in where possible, which is essential at least in winter to prevent solidification. All lines are carried by trestle or gantries fitted with pathways and hand rails, and the long lines have expansion bends every 40 to 50 yards.

Cast Iron Plug Cocks. The mild steel lines are all controlled by cast iron plug cocks with the exception of a few cast iron sluice and gate valves fitted in cases of shortage of plug cocks. On all lines $\frac{1}{2}$ " to 3" they are quite similar, being simple cast iron gland plug cocks. The plug of the cock is seated in a "pan" shell and held in position by a bolted gland packed with prepared asbestos and turned by a loose key. On all 4" lines, and some 3" lines although similar in other respects, the cocks are operated by a worm gear to facilitate turning.

The smaller cast iron gland plug cocks, $\frac{1}{2}$ ", $\frac{3}{4}$ " and 1", are double socket and screwed. The important point in connection with these cocks is to keep them properly packed, oiled and cleaned, and above all, to see that they are turned at least once every shift. In general, they are quite satisfactory and entirely safe, their life depending upon the quality of the metal. Eventually they become cracked (either plug or shell), due to the apparent

porous nature of the castings developing a fissure. All flanges are jointed with asbestos millboard and mineral jelly.

Air Releases to Pumps. Each pump is gravity fed and hence at the lowest point is prone to suffer for air lock either in the pump or the line in this vicinity of the pump. To obviate this trouble a $\frac{1}{2}$ " mild steel line controlled by a $\frac{1}{2}$ " cast iron gland plug cock is tapped into the highest point of the pump body through a special "boss." This line leads into a common 1" line to each battery of pumps which dips into a carboy or drum. After starting to pump, should a "knocking" occur due to air lock, the air release cock is opened and the air, together with a small quantity of the acid being pumped, is released, the latter being saved in the drum—this drum being then dumped at one of the dumps previously mentioned.

Earthenware Pipe Lines. These are for the weak nitric acid and lead from all such receivers at the producing plants to the mixing houses. They are mainly 3" with 2" leads, all being acid-resisting stoneware with the usual spigot and socket joint made with blue putty asbestos cord and silicate finish. To the present air locks, a Harts condenser tube is fitted vertically, open to the atmosphere.

Earthenware Plug Cocks. At the receivers they are usually 1" or $1\frac{1}{2}$ " bib cocks, the line cocks being 2" or 3" fullway. On the 3" lead lines they are 3" fullway block type with metal bolted fittings, the plugs of these being square for a key and are held down by a metal stirrup. As is expected with weak nitric acid, these cocks are liable to drip. However, they receive special attention, being greased and reseated as often as required, any drips being caught in an earthenware or lead tray leading to a carboy, from which the acid is transferred to earthenware eggs at the retorts.

Lead Acid Lines. All strong nitric acid should be fed from the strong nitric acid receivers of the producing plants to each mixer by a 3" lead line of 12-lb. chemical lead with regulus metal flanged joints or heavily burned joints. The line is controlled by the above mentioned 3" fullway earthenware block cocks and fittings. To prevent air locks a 1" vertical lead line with an anti-splash globe is led out at intervals to a height of 8 feet, i. e., above

the height of the receivers. The reason for this is obvious.

Dip Rods are in use with every storage vessel having any connection with the mixing subsection. For mixed acid and sulfuric acid storage tanks and blenders, they are made of the approximate standard lengths (e. g., for 20' x 12' tanks 14' 6", for 30' x 9' tanks 10' 6") and are of $\frac{3}{4}$ " square iron rod in feet, inches and one-half inches to the required height. They are suspended by chains from tripods over the dip holes of the respective storage tanks, there being certain advantages of having these rods tipped with aluminium to prolong their life. In dipping both strong and weak nitric acid and all acid mixtures, a copper rod is used, which is afterwards placed against an accurate lead scale.

Dipping. The success of the mixing section depends in a large measure upon accurate dipping by reliable operatives. All acid is dipped in its storage before any transfer is attempted, which is absolutely vital and equally so is the resultant dip at either end of the transfer. Detailed records, of course, should be kept of all process dips by the respective operatives and all transfers made, if necessary, can be traced back should any apparent discrepancy occur.

Sampling is equally important. Average samples of oleum are always taken from the delivery line. Samples are withdrawn from the blenders as desired by means of a lead jug suspended from a chain or lead covered rod. The jug should first be rinsed out with the acid and then the bottle for the sample rinsed out (with the acid being sampled), the fluid being withdrawn from the center of the tank. The bottle is carefully stoppered and wiped round clean, labeled and an advice note made out to accompany it to the laboratory for analysis.

Draught. For ventilation purposes to eliminate fumes, a small absorption tower with air injector is advisable. In the mixed acid house a fume line should be run into the line leading to the retorts absorption system having large air injectors. A draught for nitrocotton mixing acid tank is also advisable.

Calibrations. The true calibration of every acid containing vessel is, of course, of the utmost importance and must be accurately known. From the water calibration of each tank, the acid content is determined by means of the difference in gravity, definite amounts (usually $\frac{1}{2}$ or 1 ton) of water are run into the

tank, after being accurately weighed on a true weigh bridge, and successive dips taken. When full the tank calibration is further checked by running off similar quantities, carefully weighing them, and taking successive dips. The mixing process, theoretically, does not involve any actual loss of acid except due to accident or fume mains, hence when apparent discrepancies in transfer of acids occur, they are invariably traceable to faulty dips, slight differences in calibration perhaps controlled by temperature, but not allowed for, or more probably to fluctuating line contents which unquestionably exist to a certain extent.

Absorption Towers perform the function of absorbing any nitrogen oxides in the fumes. The usual small quartz packed towers are efficient for this purpose, being 15" in diameter and 12' high.

Nitration and Nitrous Fume Poisoning. In the study of occupational diseases and accident prevention in the chemical industries, the fume hazard and effect of nitrous fumes on the workmen; the fallacy of believing that certain men are idiosyncratic to the extent of immunity to nitrous fumes; medical supervision and treatment; prevention of fume poisoning; hygienics of correct ventilation; are exceedingly important topics, but hardly within the province of this work for profitable discussion.¹

The use of rubber aprons, boots, gloves with gauntlets and efficient goggles, coupled with an efficient ventilation wherein the fumes are removed by steam jet suction from *near the floor*, together with the insistence of proper sanitary precautions as to change of clothing, compulsory periodic bathing and periodic change in occupation, have generally been found sufficient. When acid is spilled it should at once be removed—if possible—by means of a hose and heavy stream of cold water. If this is impractical, then impure soda ash in excess should be sprinkled on, until effervescence ceases.

Calculation of Acid Baths. The regeneration of acid baths constitutes one of the most important processes in the industry of nitrocellulose. As nitration proceeds and the nitrating bath becomes higher in water and sulfuric acid and lower in nitric

1. In this connection reference is made to a comprehensive article in *Travelers' Standard*, 1918, 6, 81-97; abstr. C. A. 1918, 12, 2442. C. Duisberg, *Zts. ang. Chem.* 1897, 10, 492.

acid percentage, such baths are no longer useful for further nitration until brought back to its original composition in nitric and sulfuric acids, which is done by adding a definite quantity of concentrated rectifying acid. The quantity required for this purpose must be found by calculation in order to obviate the tedious and laborious trial methods formerly in use. Not only must the acid be brought back to its original composition, but those imperceptible irregularities accumulated during the nitration reaction to such an extent as to produce appreciable effects upon the composition of the waste acid have to be taken into consideration.

In the purifying of these acids calculations are unavoidable and by the use of graphic methods, as described herein, the troublesomeness of these calculations may be reduced and the maximum amount of time saved as the result. The frequently occurring problem in practice consists in the calculation anew of the percentage composition of the acid bath of known content after a certain proportion of sulfuric and nitric acids have been added separately or mixed together for the sake of reinforcement.

Assuming the following problem presents itself; in which it is necessary to regenerate in the nitration room, an acid bath weighing 3500 kilos, and having the following composition:

H_2SO_4 61.25%

HNO_3 23.12%

H_2O 15.63% (Including HNO_3)

If there is added, for instance, 720 kilos H_2SO_4 95%, and 350 kilos (nitric) HNO_3 89%, what will be the percentage content of the new bath, after the mixture has been effected?

In the calculation of this problem abbreviations involving the following are necessary:

- B Weight of the old bath.
- S Weight of the rectifying sulfuric acid.
- N Weight of the rectifying nitric acid.
- W Weight of the rectifying water.
- a Percentage of sulfuric acid in old bath.
- b Percentage of nitric acid in the old bath.
- c Percentage of water in the old bath.
- x Percentage of sulfuric acid in the new bath.
- y Percentage of nitric acid in the new bath.
- z Percentage of water in the new bath.
- n Strength of the rectifying nitric acid.

Problem 1. How much sulfuric acid is present in the old bath?

$$\text{Formula: } \frac{B \times a}{100} = \text{H}_2\text{SO}_4 \text{ (content of old bath).}$$

$$\text{Example: } \frac{3500 \times 51.25}{100} = 2143.75 \text{ kilos H}_2\text{SO}_4.$$

Problem 2. How much H_2SO_4 is contained in the 720 kilos of rectifying sulfuric acid?

$$\text{Formula: } \frac{S \times s}{100} \text{ content H}_2\text{SO}_4 \text{ in rectifying sulfuric acid.}$$

$$\text{Example: } \frac{95 \times 720}{100} = 654 \text{ kilos H}_2\text{SO}_4.$$

Both added together give the sulfuric acid content of the new bath.

$$\frac{B \times a}{100} + \frac{S \times s}{100} = 2827.75 \text{ kilos.}$$

The percentage composition is then easily found from the following proportion:

$$\frac{\text{Weight of the new bath}}{\text{H}_2\text{SO}_4 \text{ content of the new bath}} = \frac{100}{X}$$

or:

$$\frac{\frac{B + S + N}{\frac{B \times a}{100} + \frac{S \times s}{100}}}{100} = 100$$

from which follows:

$$(B + S + N) x = (B \times a + S \times s)$$

The percentage H_2SO_4 content of the new bath is therefore equal to,

$$x = \frac{B \times a + S \times s}{B + S + N} \quad \text{I}$$

In a similar manner is calculated the percentage HNO_3 content of the new bath:

$$y = \frac{B \times b + N \times n}{B + S + N} \quad \text{II}$$

Thus is answered the question as to whether the desired composition of the bath can be thereby attained or not. If this is not the case it becomes necessary to try with other numerical values of S and N, hence the rectification of the nitration method is determined rather by trial—by a kind of approximation method.

This procedure is undoubtedly still used in many nitrating plants, but the rapidity of the results obtained depend largely upon the guessing ability of the person entrusted therewith. The above calculations show a method for the direct determination of the quantities of rectifying acid S and N without the roundabout way of the trial method, the only question being to solve the above equations for N and S which are now unknown, whereas in this case one may assume x and y as known.

From Formula I it follows directly:

$$N = \frac{B(a - x) + S(s - x)}{x} \quad \text{III}$$

In the same way it follows from Formula II:

$$B \times b + N \times n = y(B + S + N)$$

$$\text{Hence} \quad S = \frac{B(b - y) + N(n - y)}{y} \quad \text{IV}$$

The above formulas are fundamental for all the further theoretical considerations, but whereas the formulas are comparatively simple enough the calculations involved are not satisfactory to the practical man.

L. Clement and C. Rivieré¹ have endeavored to simplify these formulas and have done so to the extent of obviating the necessity of solving the equation with two unknown quantities containing numerous figures, but the impossibility, or rather difficulty, of comprehending it at a single glance readily leads to errors of calculation.

These formulas may be elucidated by explaining in detail the following definite steps: If one tries, for instance, to solve the proposition 1000 kilos of a nitrating bath of composition 63.46% sulfuric and 20.64% nitric, to be transformed into a mixed acid containing 60.95% sulfuric and 23.08% nitric by adding 89% nitric acid and 95% sulfuric acid, it will be found by the equation that N equals +30 and S equals -20; in other words, we must withdraw 20 kilos of sulfuric acid and add 30 kilos of nitric acid—an impossibility. We therefore have recourse to graphic methods, for in this manner calculation as to working methods may be provided and time, vexation and losses eliminated. This,

1. Caout. et Guttap. 1909, May. Mon. Sci. 1913, 78, 73; C. A. 1913, 7, 1610.

however, in some instances, may be attained only in the round-about manner, through theory, particularly through the elucidation of Equations III and IV, which serve as the basis for the theoretical deductions.

Acid Calculation by Method of Clement and Rivieré, who, in the various refinements of their graphic method for calculating the nitrocellulose and nitration baths, have shown that the degree of nitration (n) is a function of the water content of the acid mixture. This, mathematically, is expressed as follows:

$$Z = \frac{140a - (9A - 2B)na - 180(A - B)n}{(9A - 2B)n}$$

A = wt. of nitrocellulose with $n\%$ N; B = wt. of acid bath; a (or modulus of nitration) = $\%H_2O$ in spent acid (Z); minus $\%H_2O$ in original bath (Z). The ratio A/B is practically a constant for any given product:

In the application of Formulas III and IV, magnitudes x and y , s and n and B may be considered as constants:

1st. x and y : Because in every bath the nitration is always carried out according to a definite formula;

2nd. s and n : Because for technical and economical reasons the rejuvenation of baths must be carried out with as concentrated acids as obtainable and which it is policy to obtain always of approximately the same strength.

3rd. B : Because the tendency in the most modern practice is to maintain a constant quantity of mixed acid. The magnitudes, therefore, a and b , are variable, while B and S are unknown.

During nitration assume the following have been used, respectively:

| | | | |
|--------------------------------|-----------|-------|------------|
| HNO ₃ | 2.463 kg. | × 5 = | 12.315 kg. |
| H ₂ SO ₄ | 8.740 kg. | × 5 = | 43.700 kg. |
| H ₂ O | 2.093 kg. | × 5 = | 10.465 kg. |

For a second nitration under the same conditions there are, therefore, necessary: 66.500 kg. of acids less 30.500 kg., i. e., 36 kilogrammes of a mixture containing, respectively:

| HNO ₃ | H ₂ SO ₄ | H ₂ O |
|------------------|--------------------------------|------------------|
| 12.315 kg. | 43.700 kg. | 10.465 kg. |
| 2.882 kg. | 21.258 kg. | 6.359 kg. |
| <hr/> 9.433 kg. | <hr/> 22.442 kg. | <hr/> 4.106 kg. |

By means of fresh acid this composition may readily be

obtained. As far as possible sulfuric and nitric acids should be employed containing the maximum percentage of monohydrate, so as to reduce to a minimum the increase by weight of the mixture recovered.¹

The initial bath is of fixed composition determined at the commencement of the nitration series, and from time to time a portion only is discarded or sold. All the factors involved in properly fortifying the bath by the use of acid mixtures of minimum cost are thus comprehended.²

The Redpath Method of Acid Calculation. The following graphical method for the determination of the quantity of fortifying and sulfuric acids to be added to preliminary mixings was communicated by the late Leon W. Redpath and first published in 1911.³ As devised by him it assumes that the concentration of the various components in the fortifying acid, the percentage composition desired in the final mixing, and the total number of pounds of acid in the preliminary mixing are constant. If the conditions conform to these specifications, the results will be mathematically correct; but should the conditions deviate from these specifications a proportional error will be introduced. However, under working conditions the error so introduced will be within the limits of error allowed for the chemical determination.

The method requires the preparation of two charts. Fig. 135 determines the effect upon the composition of the preliminary mixing caused by the further addition of fortifying acid.

It is first necessary to make a calculation to determine the effect produced upon the components of the preliminary mixing by the further addition of 1,000 pounds of fortifying acid.

Let a = the per cent. of one component of the fortifying acid.

b = the per cent. of that same component as desired in the final mixing.

c = the total number of pounds to be adjusted.

Then

$$\frac{a - b}{c} = \text{the effect produced upon that component in the}$$

1. Mon. Sci. 1913, 78, 73; abst. Wag. Jahr. 1913, 59, I, 456; C. A. 1913, 7, 1810; Kunst. 1913, 3, 203.

2. Caout. et Guttap. 1909, 6, 3185, 3269; abst. Kunst. 1912, 2, 384; C. A. 1913, 7, 257.

3. First published in 1911 by E. Worden, "Nitrocellulose Industry," 1, 138.

preliminary mixing by the addition of one pound of fortifying acid.

For example: If the sulfuric in the fortifying acid has a concentration of 41.8%, and if the concentration of the sulfuric acid desired in the final mixing is 56.50%, and if the total quantity of acid used in the preliminary mixing is 54,000 pounds, then

$$\frac{41.80 - 56.50}{54,000} = -0.000272.$$

Or, the addition of 1,000 lbs. of fortifying acid would have altered the strength of the sulfuric acid 0.27%.

The second calculation is made by the same method to determine the effect upon the nitric by the addition of 1,000 lbs. of fortifying acid to the preliminary mixing.

Assuming that the nitric in the fortifying acid is 52.40%, and that 28.2 is desired in the final mixing, then

$$\frac{52.40 - 28.20}{54,000} = 0.000446,$$

which will be the effect upon the nitric of the preliminary mixing by adding 1 lb. of fortifying acid to it. The addition of 1,000 lbs. of fortifying acid would, therefore, alter the composition by 0.45%.

It will be noted that the effect indicated upon the sulfuric acid is a minus quantity. This indicates that in the addition of fortifying acid, the sulfuric component is decreased, which we know to be the case.

Chart A (Fig. 137) is now plotted with these figures as a basis. Selecting a point near the center of a sheet of cross-section paper, and taking the origin at the top, the quantities, representing the number of pounds of fortifying acid to be used are set off downward, according to some convenient scale.

- Quantities indicating the desired change in composition of the preliminary mixing are set off to the right and to the left.
- The decreasing composition of the component will be taken as indicated by the direction to the left, while increasing composition is indicated by the direction to the right. A point set off upon the 1,000-lb. line and to the left, according to a change equal to 0.27% (calculated above), is connected by a straight line

with the origin. A point upon the 1,000-lb. line to the right, equivalent to a change of 0.45%, is also connected with the origin by a straight line. The right-hand line now indicates for all positions the relative alteration of the nitric acid in the preliminary mixing for the addition of a corresponding number of pounds of fortifying acid. The left-hand line indicates the change in the

composition of sulfuric acid of the preliminary mixing for a corresponding addition of fortifying acid.

Chart *B* (Fig. 138) is made in a similar manner, but is drawn upon tracing cloth. The origin in this case is taken at the bottom of the paper, and the minus quantities are plotted upward to the right, while the positive quantities are plotted upward to the left.

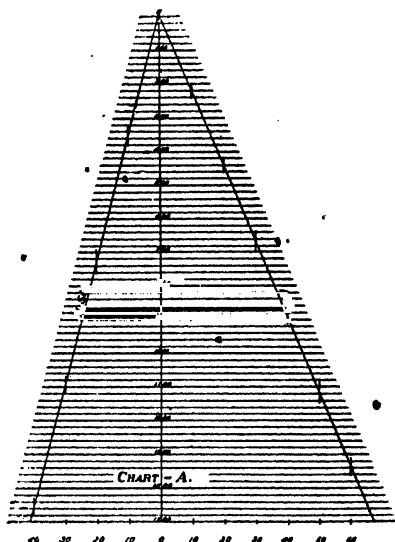


FIG. 137.—CHART *A* FOR THE REDPATH GRAPHIC METHOD OF NITRATING ACID CALCULATION

Assuming the straight sulfuric to have been 97.3% H_2SO_4 , by similar calculation the addition of 1,000 lbs. of sulfuric acid would raise the sulfuric component 0.76%, while it would have lowered the nitric 0.52%.

By superimposing Chart *B* (Fig. 138) upon Chart *A* (Fig. 137), it is possible to read by inspection the number of pounds of fortifying acid and of straight sulfuric acid which should be added in order to produce the required adjustment of the preliminary mixing.

The action of the two charts is perhaps best seen by assuming a case of the addition, for instance, of 400 lbs. of fortifying acid and 200 lbs. of sulfuric acid, and observing the relation between

the two charts. Place the 200-lb. line of Chart *B* (Fig. 138) directly over the 400-lb. line of Chart *A* (Fig. 137), and in such a position that the intersection of the left-hand diagonal with the respective pound lines coincide. It will be observed that during the addition of the 400 lbs. of the fortifying acid the sulfuric acid has fallen in concentration 0.11%, and that from the addition of 200 lbs. of sulfuric the sulfuric component is raised 0.15%. The algebraic sum of these two quantities, an increase of 0.04, will be found to be indicated by the position of the origin on Chart *B*, its position now lying 0.04 to the right of the neutral line of Chart *A*.

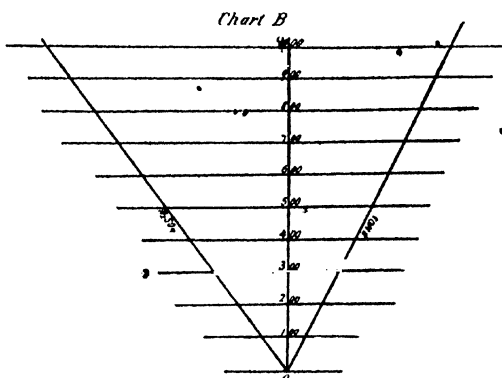


FIG. 138.—CHART *B* FOR THE REDPATH GRAPHIC METHOD OF NITRATING ACID CALCULATION

Simultaneously, it will be found that during the addition of 400 lbs. of fortifying acid, the nitric component was raised 0.18%; but that during the addition of the 200 lbs. of sulfuric this component diminished 0.11%, a net decrease of 0.07%. This position on *A* will be found at a distance of 0.03 to the right of the position of the origin of Chart *B* as it is now situated. It will also be found that there is the same distance of 0.03 at the level of the 200-lb. line on Chart *B* between the right-hand diagonals on Charts *A* and *B*. Had the diagonal on Chart *B* been continued from the intersections of the diagonal on *A* with its 400-lb. line, and had it been continued downward with its own "slope" from this point, the line thus assumed, parallel to the diagonal on *B*, would

have intercepted the base line at a position 0.03 to the left of the origin on *B* or 0.07 to the right of the neutral line of *A*; 0.07 being the algebraic sum of the alteration caused in the HNO_3 component by the addition of 400 lbs. of fortifying and 200 lbs. of sulfuric, while the 0.03 is the algebraic difference between the resultant effect upon the sulfuric and nitric and components by the additions so made.

This example which we have just considered is, of course, the reverse of the usual operation. Ordinarily, from the analysis of the preliminary mixing, the required change which must be made is determined. The usual operation would then have been performed by placing the neutral line on *B* directly over that ordinate which shall represent the desired increase in the sulfuric acid component. With Chart *B* in this position, raise it and lower it perpendicularly across the surface of the chart until it shall so occur that at the level of the intersection of the two left-hand diagonals there shall be a distance between the two right-hand diagonals equal to the algebraic difference of the change desired in the two components. Thus, if it were desired to raise the sulfuric acid 0.04, and to raise the nitric acid 0.07, the algebraic difference between these two quantities would be 0.03, and the Chart *B* should be so placed that with the neutral line of *B* over +0.04 on *A* there shall be a distance equal to 0.03 between the two right-hand diagonals at the altitude of the intersection of the left diagonals.

When such a position has been found, the quantities of fortifying acid and of sulfuric acid required will be read by inspection upon Charts *A* and *B* at this same altitude.

The process of adjusting Chart *B* to its correct position will probably require about one minute, if the chart is thoroughly understood, and it will be found convenient to make use of a pair of dividers in setting off the distances required between the diagonals. It will also be found convenient to place Chart *A* upon a drawing board and to insert Chart *B* in a light frame, and to arrange some suitable guide for directing the perpendicular motion of this latter chart, then when the correct lateral position has been determined, clamp the guide, and maintaining this position, it is a simple matter to raise or lower the frame until

the correct position is discovered. This should take about 1 minute.

It may be added that while the scope of this graphical method is somewhat limited by the size of the charts, it is a simple matter to reduce these quantities to a mathematical formula; so simple that the result can be obtained almost mentally in a moment. This formula will enable mixings to be made up directly from known spent if this is desired, except for the fact that variation of the composition of the fortifying would introduce greater error.

It will be observed, therefore, that Redpath regenerates baths with the acid mixture of a definite composition and completes the work by means of sulfuric acid; whereas Clement and Rivieré bring the old bath back to its former strength with sulfuric and nitric acids separately or with one of these acids and water.

H. Schwarz¹ has obtained excellent results using the Redpath process and gives specific practical examples.² His results show

1. Zts. Schiess. Spreng. 1913, **8**, 288, 313; abst. C. A. 1913, **7**, 3664; Wag. Jahr. 1913, **59**, I, 457.

2. This requires two diagrams which are superposed. The tables must be drawn in advance for a definite quantity of old acid, say 40,000 kilograms. A further presupposition is that every time the composition of the old bath must be determined by analysis. Of course the analysis may be carried out also after a provisional correction, which is often done in practice. Furthermore, the acid mixture used for the correction must always have the same composition, for instance, 56% H_2SO_4 and 39% HNO_3 .

The HNO_3 line in the table is drawn in such a way that it indicates the increase of nitric acid in per cent., when acid mixture is added. As all these values lie approximately on the same straight line, it is easy to draw a graphic table because only the final point requires calculation. Likewise, the H_2SO_4 diagonal. It usually gives negative values, as the acid mixture used for the correction is always taken with a high HNO_3 content, which causes a falling off of the sulfuric acid in the old bath. Hence the values at the left side of the central line are negative, and those at the right side are positive.

Redpath himself has indicated a quite simple formula by means of which these variations in the percentage can be immediately calculated for any acid mixture.

H_2SO_4 % of the correction acid — H_2SO_4 % of the ideal acid divided by total weight of the acid bath gives the variation in the H_2SO_4 component caused by one kilogram of acid mixture.

If the ideal acid is, for instance, 62% H_2SO_4 , 20% HNO_3 , 18% H_2O , then the variations of the H_2SO_4 component caused by the addition of one kilogram of acid mixture will be equal to $\frac{55 - 62}{40000}$ equals 0.00015%.

If one thousand kilograms of acid mixture is added, then the H_2SO_4 content decreases by 0.15%. Hence this amount will be set off towards the left at the height of the 1,000 kilogram line; thus the point of the H_2SO_4 line will

that with ordinary manipulative skill, it is possible in practice to be determined. By connecting this point with the origin (zero point) and by prolonging this line we obtain immediately all the desired values.

The increase of the HNO_3 component is obtained in a quite similar manner as follows:

HNO_3 — content of the correction acid — HNO_3 — content of the ideal acid divided by the total weight of the acid bath gives the variation in the HNO_3 — component by the addition of 1 kilogram of acid mixture.

For example, it will be found: $\frac{39 - 20}{40000} = 0.000475\%$.

This means an increase of the HNO_3 of 0.47% per 1000 kilograms of acid mixture.

In quite similar manner Table B is obtained. Only one begins to set off from below upwards. For the sake of verification or practice it is advisable to transfer this table upon tracing paper. In this table, which of course must be drawn to the same scale as Table A, the horizontal distances from the central line indicate the deviations: H_2SO_4 at the left and modifications in the HNO_3 content at the right when only H_2SO_4 is added to the old acid. One would find, therefore, that 1000 kilograms of sulfuric acid with a 96% content increases, according to the above formula, the H_2SO_4 component of

the bath by $\frac{96 - 62}{40000} \times 1000$ equals 0.85%—and lowers correspondingly the

HNO_3 component by $\frac{0 - 20}{40000} \times 1000 = (-) 0.5\%$. This is all that is

necessary for the establishment of Table B. Now if the two diagrams are superposed, it is found what changes occur in the original acid mixture when it is rectified simultaneously with fresh acid mixture and sulfuric acid.

If one takes 1000 kilograms of acid mixture and 1000 kilograms of sulfuric acid for the purpose of rejuvenation, then the 1000 kilo line of diagram B is placed upon the 1000 kilo line of diagram A, when the variations in the percentage of the original bath are read off directly.

If we consider first the two diagonals of the left side at the height of this 1000 kilogram line, then we read:

1000 kilograms of acid mixture lowers the H_2SO_4 content by 0.15%.

1000 kilograms of H_2SO_4 raise the H_2SO_4 content by 0.85%.

If both are added simultaneously one may note an increase of the H_2SO_4 component, which is equal to the difference of these two values or to 0.7%. This amount can be read off directly and is equal to the distance of the two diagonals on the 1000 kilogram line. The reading is done still more conveniently if one shifts the two diagrams horizontally until the two diagonals intersect at the height of the 1000 kilogram line. The distance of the two central axes from A and B gives the looked-for value of 0.7%. The central axis B is at the right side of A, hence the value is positive.

In a similar manner is taken the reading at the right side with reference to the HNO_3 components:

1000 kilograms of acid mixture raise the HNO_3 content by 0.475%.

1000 kilograms of H_2SO_4 lower the HNO_3 content by 0.0500%.

Now if, in order to make the reading as simple as possible from the beginning, the diagram is so shifted that the two diagonals of the right side intersect at the height of the two thousand kilograms lines, it will be seen that the central axis B is situated at the left side of the central axis A, namely, at a distance of 1.025%. This is therefore equal to the negative difference of the above figures. In other words, the nitric acid component has fallen off by 0.025%. The above examples are the exact opposite of that which is ordinarily in operation. It will not therefore be superfluous to illustrate by

make the calculations in a determination of the components of means of such a "reversed" example how one must proceed in practice.

1. Simplest case: Let us assume that the analysis of a working sample gave the following results:

62.11% H_2SO_4 and 19.67% HNO_3 . We desire, therefore, a decrease of H_2SO_4 of 0.11%; Increase of HNO_3 of 0.33%. As in practice the case in which the correction is to be obtained by adding only acid mixture is not rare, it is advisable to observe first whether diagram A alone does not give the answer. In fact, in our example a glance at diagram A shows that the object can be obtained with 700 kilograms of acid mixture.

(2) Example in which both diagrams are required:

Working acid: 62.06% H_2SO_4 and 19.46% HNO_3 . We desire a decrease of H_2SO_4 of (-) 0.06%; increase of HNO_3 of (+) 0.54%. Algebraic difference 0.60%.

For this purpose one should proceed in the following manner: The central line of B should be placed directly over the ordinate which corresponds to the desired increase in the sulfuric acid component, that is, over 0.06 at the left side because the figure is negative. At any rate the diagram B must remain in this position. Then the algebraic difference 0.60 is taken with the compasses and the diagram B is shifted upwards or downwards until, at the height of the point of the intersection of the two diagonals, the distance between the two right diagonals becomes equal to this difference.

This is the case as soon as the 160 kilogram line of diagram B coincides with the 1300 kilogram line of diagram A. The difference will have to be looked for below the point of intersection of the two right diagonals, because it is negative in this special case. Hence the bath (40000 kilograms) is to be corrected with 1300 kilograms of acid mixture and 160 kilograms of 90% sulfuric acid.

The use of these tables require, of course, a certain amount of practice. If, however, the principle has been correctly understood, it becomes possible to find the result in less than one minute. It is advantageous to draw diagram B upon a sheet of tracing celluloid, and also diagram A on millimeter paper stretched over a wooden support. In order to facilitate the vertical movement, one displaces diagram B along a ruler equipped with a clamp which allows of fastening diagram B in any desired position. It may also be mentioned that, owing to the small size of the two diagrams, the calculation possibilities are somewhat limited. But even in such a case it is easy to convert the results into different proportions without using any mathematical formula. If care is taken that the acid mixture, which is used for rectifying the baths should always have the same composition, then the results would always be mathematically accurate. However, not all problems can be solved. For cases may occur in which the goal is not reached by adding acid mixture and sulfuric acid. This is particularly the case when the water content of the working acid is inferior to the water content of the ideal acid, hence in our special example below 18%. An attempt with the diagram will convince us soon that an acid with 62.4% of H_2SO_4 and 20.1% HNO_3 cannot be raised to the desired height because the water content of this working acid amounts to 17.5%. It is plain that an acid mixture, like the one assumed above, will decrease the water content of an acid and not increase it. Only water can help in such cases, or a correction with the unmixed acids themselves. The thought suggests itself to construct supplementary tables for these purposes, such as for the system acid mixture plus nitric acid, or acid mixture plus water. Redpath has expressed an opinion on this point. It is found, however, that such tables cannot be constructed on the basis of Redpath's working manner, because the correc-

a nitrating acid mixture is not to exceed five or six minutes. tion with the acid mixture and nitric acid is equal in its action to the sum of the actions exerted by the single acids. He who has experience in the use of this method will see that the action of the sun is quite inconvenient and renders the construction of such a table impossible.

A brief synopsis of the actions is given below:

| 1. SYSTEM: ACID MIXTURE + H ₂ SO ₄ | | | |
|--|---|---|--------------------------|
| Action upon | Action of 1000 kilograms of said mixture. | Action of 1000 kilograms H ₂ SO ₄ | Action of both together |
| H ₂ SO ₄ | Decrease | Increase | Differential action |
| HNO ₃ | Increase | Decrease | Differential action |
| 2. SYSTEM: ACID MIXTURE + HNO ₃ | | | |
| H ₂ SO ₄ | Decrease | Increase | Summation of the actions |
| HNO ₃ | Increase | Increase | Summation of the actions |
| 3. SYSTEM: ACID MIXTURE H ₂ O | | | |
| H ₂ SO ₄ | Decrease | Decrease | Summation of the actions |
| HNO ₃ | Increase | Decrease | Differential action |

Although this could be considered, perhaps, as a weak spot in the method of Redpath, still it is easy to bring remedy by using the Clement and Riveré maps as supplementary tables. In this manner one is sure to find in the shortest possible time a solution for every possible case which is mathematically accurate.

A few problems for practice may not be superfluous, in connection with which the occurring difficulties will be cleared up. They will serve as a support for the analyst who at the beginning allows himself to be too easily confused. This appendix is the more necessary as the reading of the results by means of Redpath's diagram requires also some practice.

(1) Example in which both components are to be raised:

| | |
|--|--------------|
| Working acid 61.90% H ₂ SO ₄ and 19.49% HNO ₃ . | We desire an |
| Increase of H ₂ SO ₄ of (—)..... | 0.10% |
| Increase of HNO ₃ of (—)..... | 0.51% |
| Difference..... | 0.41% |

Place the central line B upon 0.1 at the right side of the central line A because 0.1 is positive, and take the difference 0.41 with the compasses for the measurement of the distance of the right diagonals. The left diagonals

will intersect at the height of : 1500 kilograms of acid mixture
400 kilograms of sulfuric acid.

* (2) A similar example in which, however, the difference is positive:

| |
|--|
| The working acid 61.53% of sulfuric acid and 19.79% HNO ₃ requires |
| an increase of H ₂ SO ₄ of (+)0.47%, and increase of HNO ₃ of (+)0.21%, |
| or a difference of —0.26%. |

The central line is situated at the right above 0.47 and 0.26 is taken with the compasses as a differential distance. This time it will be situated above the point of intersection of the right diagonals because the algebraic difference is now positive. The left diagonals now intersect at the height of 1260 kilos of acid and 780 kilos of H₂SO₄. In general, the triangular region comprized between the two right diagonals and situated above the point of intersection of these diagonals is the region of the positive algebraic differences, whereas the region below the point of intersection is the region of the negative differences, to which especial attention may be drawn.

It is to be noted that the signs of the numerical values of the acid components merely indicate an increase or a decrease and hence are to be set

The R. Fowler Method of Spent Acid Graph Construction.

The principles upon which this graph is constructed, as perfected by R. Fowler¹ are applicable to the revivification of any spent acids where revivifying and sulfuric acids are used. The graph will therefore be found equally useful for adjusting the strength of blends that do not come up to specifications. It is assumed that the compositions of the spent and revivifying acids vary from time to time, but that the percentage composition of the sulfuric acid remains, for practical purposes, constant. These conditions, of course, obtain in usual works practice. The actual graph to be constructed for any specified composition of nitrating acid will be a portion only of a general graph which will be first considered.

Let the percentages of H_2SO_4 and HNO_3 in the nitrating acid be x and y , respectively, in the spent acid x_1 and y_1 , and in the revivifying acid x_2 and y_2 , and the percentage of H_2SO_4 in the off to the right (+) or to the left (-) of the central axes, whereas the signs of the difference indicate in what region the distance is to be looked for, whether in the upper (+) or in the lower (-) field.

(3) The importance of this rule of signs is best shown by a comparison of two examples. Assume we have two working acids of the following compositions; I 61.65% H_2SO_4 and 19.55% HNO_3 , while II consists of 61.05% H_2SO_4 and 19.75% HNO_3 . Hence we require:

| | I | | II |
|--|-----------|-----------|----|
| Increase of H_2SO_4 of | (+) 0.35% | (+) 0.35% | |
| Increase of HNO_3 of | (+) 0.45% | (+) 0.25% | |
| Algebraic difference | -0.10% | +0.10% | |

The procedure is quite the same for both problems; the central line B is placed upon 0.35 (right) and the distance 0.10 is taken with the compasses. By shifting B upwards or downwards both solutions are found at the same time, the differential distances lying in case I in the lower or minus region, and in case II in the upper or plus region. The significance of the signs thus becomes clear.

Solution of Problem I. 1700 kilos of acid mixture, 700 kilos of H_2SO_4 .
II. 1180 kilos of acid mixture, 620 kilos H_2SO_4 .

(4) Example in which one component remains constant: Working acid, 61.71% H_2SO_4 and 20.01% HNO_3 . Desired increase of H_2SO_4 (+) 0.29% HNO_3 is to remain constant. The difference therefore is +0.29%.

The central line is situated on 0.29 (right). The difference is determined as usual with the compasses. Result is 440 kilos of acid mixture and 420 kilos of H_2SO_4 .

(5) Example which does not find any solution because the water content of the working bath (62.0% H_2SO_4) and 20.42% HNO_3 amounts to only 17.58%, hence is smaller than in the ideal bath. In this instance one must resort also to H_2SO_4 and water or to diluted sulfuric acid. In such an instance the answer is most readily obtainable by the method of Clement and Riveré.

1. J. S. C. I. 1919, 33, 34T; abst. C. A. 1919, 13, 1018.

sulfuric acid x_3 . These compositions may be shown in graphical form, plotting percentages of H_2SO_4 on abscissae and of HNO_3 on ordinates, as on Fig. 140.

For any given case x and y are both fixed quantities. Let the point (x, y) be N , and the point $(x_3, 0)$ lying on the x -axis, V . If the points V and N be joined and this line produced indefinitely, the portion produced is the sulfuric acid line.

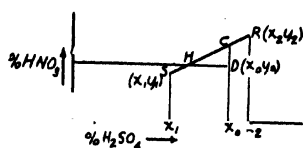


FIG. 139.—FOWLER METHOD OF SPENT ACID CALCULATION

Now x_1, y_1, x_2, y_2 vary within certain limits according to plant working. Let the points (x_1, y_1) and (x_2, y_2) for any particular case be S and R , respectively. Now the line SR will cut the line VN produced, for if not, revivification by means

of the revivifying and sulfuric acids available is impossible (see below). Let P be the point of intersection.

(In what follows an acid having a composition represented by the point S will be shortly called "S acid" and similarly for other points.)

It can be readily shown that by mixing S acid and R acid in suitable proportions, any acid of composition lying on the line SR may be made, and no other composition can be made, by mixing S acid and R acid (see Fig. 139). For if x_2 be greater than x_1 , the sulfuric acid content of any mixture of the two must be greater than x_1 and less than x_2 , that is, it must lie between x_1 and x_2 .

Similarly the nitric acid content of any mixture of the two must lie between y_1 and y_2 .

Let D be any point lying between x_1 and x_2 and also between y_1 and y_2 and let its coordinates be x_0 and y_0 . To obtain an acid whose sulfuric content is x_0 (by the ordinary rule for mixtures) S acid is to be mixed with R acid in the ratio $(x_2 - x_0) : (x_0 - x_1)$. Similarly, to obtain an acid having a nitric acid content of y_0 , S acid must be mixed with R acid in the ratio $(y_2 - y_0) : (y_0 - y_1)$. In order that both nitric and sulfuric acid contents may be satisfied $(x_2 - x_0)/(x_0 - x_1)$ must be equal to $(y_2 - y_0)/(y_0 - y_1)$. Let the ordinate x_0 cut RS at C and the ordinate y_0 cut it at H . Then $(x_2 - x_0)/(x_0 - x_1) = CR/CS$, since the ordinates are

parallel, and $(y_2 - y_0)/(y_0 - y_1) = HR/HS$ similarly. For $(x_2 - x_0)/(x_0 - x_1)$ to be equal to $(y_2 - y_0)/(y_0 - y_1)$, HR/HS must be equal to CR/CS , that is, C must coincide with H, and D must lie on SR. Therefore if R acid and S acid be mixed, the composition of the resulting blend lies on SR. Since P lies on SR, the acid represented by it may be made by mixing S acid and R acid in the proportion of the lengths of PR to PS (see Fig. 140). Similarly since N lies on PV, the acid represented by it (nitrating acid) may be made by mixing P acid and V acid in the proportions of the lengths of NV and NP.

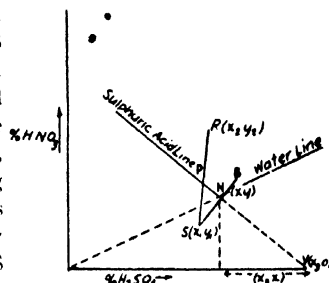


FIG. 140.—FOWLER METHOD OF SPENT ACID CALCULATION

Now since both N and V are fixed points the length of NV is constant and equal to $\sqrt{y^2 + (x_3 - x)^2}$ and the tan. of the angle that NV makes with the x axis is $y \div (x_3 - x)$.

Consider the case of a unit weight of P acid and suppose PN equal to $VN \div m$, then in order to obtain N acid, V acid and P acid must be mixed in the proportion PN to Vn, i. e., $\frac{1}{m}$ of V

acid to every unit of P acid, giving $\frac{m+1}{m}$ units of N acid.

Therefore if the line VN produced be graduated towards P with divisions each equal to $\frac{1}{z} \sqrt{y^2 + (x_3 - x)^2}$, where z is any con-

venient integer, each graduation will represent $\frac{1}{z}$ units of V acid to a unit of P acid.

Similarly if ON be joined and produced it becomes the water line. It may be divided in the same manner as the sulfuric acid

line into divisions each equal to $\frac{1}{z} \sqrt{x^2 + y^2}$. The tan. of its angle

is $\frac{y}{x}$. This may be found useful in extreme cases for blends in

which the content of sulfuric and nitric acids is high, for in such cases the line joining B (the point representing the composition of the blend) to S may not cut the sulfuric acid line and the point P will then fall on the water line. This, however, should only happen in exceptional cases, as it is obviously bad practice to add water, if it can possibly be avoided, since it involves the introduction into the system of water which must be removed at a later stage.

Now for any particular composition of nitrating acid it is plainly not necessary to construct the whole of the graph as shown on the diagram. Only that portion need be drawn as shall contain the points N, S and R (both S and R varying according to plant working), and this portion should be enlarged to a suitable size. The limits within which the composition of spent and revivifying acids vary in plant practice can readily be determined and the graph constructed accordingly. The highest nitric content in revivifying acid and the lowest in spent acid will fix the nitric acid limits, and similarly for the sulfuric acid content. The limits being fixed, the point N is found and from it in the direction of P a line is drawn making an angle having a tan. of $y/(x_3 - x)$ with the x-axis and produced right across the graph. This line is divided into equal divisions from N towards P, each division being equal to $\sqrt{y^2 + (x_3 - x)^2}/1000$ units (or some convenient multiple of it). Then each division will represent 0.001 long ton of sulfuric acid per ton of (revivifying + spent) acid. The graph is then complete.

The water line may be inserted if thought desirable. From N a line is drawn in the proper direction, as in the figure, making an angle with the x-axis having a tan. of y/x , and is divided into equal divisions each equal to $\sqrt{x^2 + y^2}/1000$ units (or some convenient multiple). Each division will represent 0.001 long ton of water per ton of (revivifying + spent) acid.

The method of using the graph is simple. The compositions of the spent and revivifying acids to be used are plotted by means of two pins; a graduated ruler is placed close to these and the distances SP and RP are noted. Then tons of spent acid \times SP/RP gives tons of revivifying acid required. And (tons spent + tons revivifying acid) \times reading on the sulfuric acid (or water) . .

line gives tons of sulfuric acid (or water) which are required.

When using the graph for adjusting the strength of blends that do not come up to specifications, the point B is plotted representing the composition of the blend. (a) If B falls on either the sulfuric acid or the water line the addition required is immediately read off, for tons of blend \times reading gives tons of sulfuric acid or water required. (b) If B falls above the sulfuric acid (or water) line the blend may be mixed with spent acid in the same manner in which revivifications are made. (c) If B falls below the sulfuric acid (or water) line, revivifying acid may be used in the same manner in which revivifications are made.

Example. It is required to construct a graph for the revivification of spent acid varying in composition between 19% and 24% HNO_3 and 60% and 62% H_2SO_4 . The revivifying acid produced on the plant varies between 28% and 32% HNO_3 and 59% and 63% H_2SO_4 . The nitrating acid is to be 62.15% H_2SO_4 and 23% HNO_3 and the sulfuric acid available contains 93% H_2SO_4 . The limits of the graph are in this case 19% to 32% HNO_3 and 59% to 63% H_2SO_4 , and therefore a scale of 1 inch to 1% will be convenient. The tan. of the angle that the sulfuric acid line makes with the x axis $\frac{y}{x_3 - x} = \frac{23}{93 - 62.15} = \frac{23}{30.85}$. The sul-

furic acid line can then be drawn. If considered necessary the water line can be inserted as well. The tan. of its angle is $\frac{y}{x} = \frac{23}{62.15}$. The divisions must now be marked off on the sulfuric acid line. Each is to be $\sqrt{y^2 + (x_3 - x)^2} \div 1000$ inches, i. e., approximately $\frac{1}{26}$ in. Consequently if divisions of $\frac{1}{18}$ inch be marked off they can be numbered 0.002, 0.004, 0.006, etc. The divisions on the water line are to be $\sqrt{x^2 + y^2} \div 1000$, or nearly $\frac{1}{18}$ inch.

An example of a revivification by the above graph is given. Spent acid 60.9% H_2SO_4 , 20% HNO_3 ; revivifying acid 61.4% H_2SO_4 , 28.9% HNO_3 . The distance PS is 96 mm. and RS is 130 mm. The sulfuric acid reading is 0.034. Therefore 100 tons of spent acid will require $100 \times 96 \div 130 = 73.85$ tons of revivifying acid, and the amount of sulfuric acid required will be $173.85 \times 0.034 = 5.91$ tons. A reduced sketch of the above

graph is given in Fig. 141, with an illustrative example shown.

In practice the graph is mounted on a sheet of composition board strengthened with an edging of batten and covered with tracing cloth to preserve it. When the pin-holes become too numerous the tracing cloth is renewed.

The graph is approximately 14 by 8 inches and any con-

stituent can be readily calculated to within 0.02% in the nitrating acid.

The Craven Method of Acid

Calculation. In establishments where sulfuric acid is largely used and where mixtures of oleum and concentrated oil of vitriol are frequently made, E. Craven¹ has suggested a simple device for graphically determining the proportion of the two acids to use to obtain an acid of given concentration. His device consists of a wooden panel sliding between two scales, one for oleum in 1% SO_3 and the other for C. O. V. in % H_2SO_4 , whereby it is possible to directly read off the desired quantities.

Analysis of Mixed and Spent Acids.

The following reliable methods for determining the nitrous, nitric and sulfuric acids in mixed and spent acids

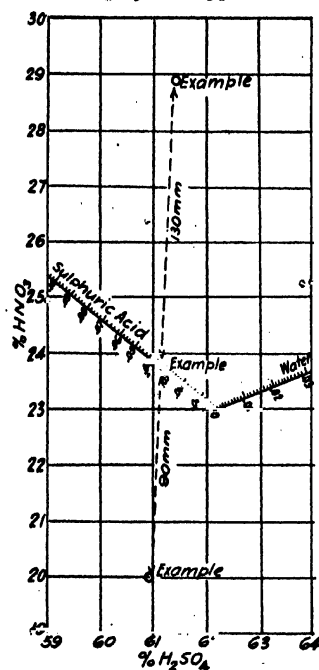


FIG. 141.—FOWLER METHOD OF SPENT ACID CALCULATION

have been selected for their simplicity and rapidity of execution as being especially applicable to factory practice.

(1) The total acidity is determined by a 2 cc. sample, the weight of which has previously been ascertained by weighing the contents of a 100 cc. picnometer of the acid to be examined.

1. Chem. News, 1918, 117, 217; abst. C. A. 1919, 13, 249. See D. Lopez and A. Swanson, Chem. Met. Eng. 1918, 19, 816; abst. C. A. 1919, 13, 263.

The sample is opened under water, rinsed out, and made to a definite volume (say 100 cc.). An aliquot portion is titrated with semi-normal sodium hydroxide, properly standardized.

The sulfuric acid is obtained from a portion of the above by gravimetric precipitation with barium chloride as described under "Estimation of Sulfuric Acid."

Nitrous acid is estimated by diluting a portion of a known weight of the sample, neutralizing with sodium hydroxide or carbonate, then treating with potassium ferrocyanide and citric acid. The total acidity found, less the sum of the nitrous and sulfuric acids found, represents the amount of nitric acid present.

(2) The specific gravity is determined by means of a hydrometer or (preferably) a picnometer, and the oxides of nitrogen by the permanganate method as described elsewhere. The total acidity is then determined by titration as indicated in (1) above, this acidity being calculated into nitric acid. Next, determine the nitric acid by the nitrometer, subtract this percentage from the total acidity, the difference being sulfuric acid.¹

(3) Method of F. Mihr.² Mixed acids, both fresh and spent, may be determined by this method to an accuracy of 0.1% without the use of the nitrometer. The total acids are first determined by titration with standard alkali, the nitric acid is then driven off by heat, after which a second titration gives the amount of sulfuric acid present. Subtraction of the sulfuric acid found from the total acidity gives the percentage of nitric acid in the sample under examination. If nitrosylsulfuric acid is present it must be decomposed by the addition of water before evaporation on the water-bath commences. Several evaporations may be necessary, small amounts of water being added each time, and the evaporative process continued until the water vapor has lost the smell of nitric acid, and does not redden moist blue litmus paper held in the escaping vapor. The presence of organic matter³

1. The calculation of results would be as follows: Total acidity, say, 96.2%; nitrogen by nitrometer, 16.8%; difference, 79.4%. Then $\frac{79.4 \times 49}{63} =$

61.76% H_2SO_4 , 49 being one-half the mol. wt. of H_2SO_4 and 63 the mol. wt. of HNO_3 . Cf. A. Van Gelder, J. S. C. I. 1900, 19, 508, 645; 1901, 20, 339; abst. J. C. S. 1900, 76, ii, 621; Chem. Centr. 1900; 61, II, 444, 643; 1901, 62, I, 1341; Chem. Tech. Rep. 1900, 39, 795; Chem. Ztg. Rep. 1900, 24, 207; Jahrb. Chem. 1900, 33, 241; 1901, 34, 266.

2. Chem. Ztg. 1907, 31, 324, 340; abst. C. A. 1907, 1, 1488; Zts. ang. Chem. 1907, 20, 1951.

(dissolved cotton and the lower nitrocelluloses), nitrogen oxides, ferrous sulfate, lead sulfate and nitrocellulose scarcely effect the accuracy of the results.

Lunge and Berl¹ state that this value gives results for nitric acid that are too high on account of loss of sulfuric during evaporation, but such possible losses are negligible if the evaporation is conducted quietly, and loss of acid from spurting is guarded against. Attention is called to the fact that this method for nitric acid is preferable to the nitrometer method for waste acid containing small amounts of nitrocellulose in solution and suspension that readily yield up their nitrogen in the nitrometer. Where the evaporation is conducted at low temperatures and water added once or twice during evaporation, very concordant results are obtained comparable in accuracy with the nitrometer, especially for unused mixed acids.

(4) *Method of Lunge and Berl.* (a) The total acidity is determined by weighing off two to three grams in a bulb pipette, the contents allowed to cautiously flow into a large volume of cold water, and the bulb thoroughly rinsed out. The total acid is then estimated by titration with *N*/1 NaOH. If litmus or azolitmin is used as an indicator, prolonged boiling is necessary; methyl orange may be employed notwithstanding the nitrous acid present if the titration is carried out in the cold and the indicator either renewed during titration, or else added just before neutralization. Or, the standard sodium hydroxide may be added in excess, then the indicator and the excess of alkali titrated back to neutrality and allowed for.

(b) The lower nitrogen oxides are determined by allowing the acid to flow into a known amount of standard potassium per-

1. Zts. ang. Chem. 1905, **18**, 1681; 1908, 340; abst. Wag. Jahr. 1908, **54**, I, 454. In the electrical conductivity method of analysis of mixtures of nitric and sulfuric acids as worked out by H. Corvazier (Mon. Sci. 1912, **76**, 322; abst. J. S. C. I. 1912, **31**, 487) the mixed acid is first titrated with baryta solution in order to determine the amount of the two acids together, and then the electrical conductivity of the solution is measured at intervals while a standardized solution of sodium carbonate is being added. The conductivity falls slowly at first and then, after the barium nitrate is completely converted into carbonate, increases rapidly. The results are plotted and from the slope of the two branches of the curve the exact point at which the whole of the barium is precipitated is obtained by interpolation. The number of cc. of sodium carbonate corresponding to this point is equivalent to the nitric acid, and the sulfuric acid is then calculated by difference. The results are claimed to agree well with those obtained by the evaporation method.

manganate solution. A standardized semi-normal potassium permanganate solution is employed, the sample under examination being always added to the permanganate and never conversely. The titration is carried out by allowing the sample to flow from a glass-stoppered burette into a known volume of the standard permanganate solution previously diluted with five volumes of water at 30°–40°, until the color just fades. The amount of permanganate required varies with the nitrous content of the sample under examination, one cc. permanganate corresponding to 0.0095 N_2O_3 . The nitrogen may be calculated as HNO_2 , N_2O_3 or NO_2 . The lower nitrogen oxides present in the strong nitric acid consist mainly of NO_2 , which, upon mixing with concentrated sulfuric acid this is converted into equimolecular proportions of HNO_3 and $SO_2(OH)(ONO)$. In the case of calculation to NO_2 , each cc. of $N/2$ $KMnO_4$ is equivalent to 0.023 gm. NO_2 . If, therefore, x represents the number of cc. of permanganate solution taken, y the cc. acid required for decoloration, and s the sp. gr. of this acid, then the NO_2 content in gm. per liter is equal to $\frac{23.00 x}{y}$ or in percentage by weight, $\frac{2.30 x}{ys}$.

(c) The total nitrogen acids are determined by the nitrometer, the value found, minus that found in determination (b) representing the nitric acid content, while (a) — (c) gives that of the sulfuric acid.

(d) Estimation of the sulfuric acid is made by weighing off 2–3 gm. of the sample in a bulb pipette, transferring to a porcelain evaporating dish and heating on the water-bath as previously described, water being added during the evaporative process to destroy the nitrosylsulfuric acid. Heating is continued until no nitrous fumes can be detected upon rotating the dish. The contents are then washed into a beaker and titrated with semi-normal NaOH with methyl orange or azolitmin as indicator.

(5) *Method of G. Finch.* The total acidity is determined by titration; the nitrous acid by permanganate. About 10 gm. of the acid mixture is diluted to one liter, 50 cc. titrated with $N/10$ barium hydroxide, using one drop of phenolphthalein indicator, boiled and filtered. The filtrate, containing barium nitrate and nitrite, is titrated, boiling with perfectly neutral, CO_2 -free potassium chromate solution. The barium chromate rapidly settles.

and the yellow color of the excess potassium chromate serves as the end-point. The barium hydroxide used equals the total acidity and the barium chromate the nitrous and nitric acids. Nitrous is found by titration with potassium permanganate of twentieth normal. From these values the nitric and sulfuric acids are readily calculated.¹

(6) *Method of G. Coffei and G. Maderna.*² The total acidity is determined by diluting 2-3 gm. of the acid with $N/2$ NaOH solution and methyl orange, after diluting the acid to about 100 cc. Sulfuric acid is determined gravimetrically with barium. Nitrous acid is estimated by diluting a portion of the acid mixture, neutralizing with sodium carbonate and treating with potassium ferrocyanide and citric acid. The difference between the quantity of sulfuric and nitrous acids and the total acidity represents the nitric acid.³

T. Chandelon⁴ has called attention to a possible source of error in the analysis of waste acids from the nitrocellulose manu-

1. Zts. Schiess. Spreng. 1912, **7**, 113, 337; abst. J. S. C. I. 1912, **31**, 358, 1028; C. A. 1912, **6**, 2375. Zts. Schiess. Spreng. 1912, **7**, 388; abst. C. A. 1913, **7**, 388. See W. Fischer and N. Steinbach, Zts. anorg. Chem. 1912, **78**, 134; abst. J. C. S. 1912, **102**, ii, 1093. H. Corvazier, Zts. anorg. Chem. 1912, **78**, 133; J. C. S. 1912, **102**, ii, 1092; Mon. Sci. 1912, (5), **2**, I, 322.

2. Gaz. chim. ital. 1907, **37**, I, 595; II, 13; abst. J. S. C. I. 1907, **26**, 1008. C. A. 1909, **3**, 72. For the estimation of nitric, sulfuric and picric acids in the presence of each other, see F. Richardson, J. S. C. I. 1917, **36**, 13.

3. These authors make use of the vigorous evolution of nitric oxide on adding acetic acid to a mixture of potassium ferrocyanide and alkaline nitrite, as a basis for a method for the determination of nitrous acid. The method is carried out with the aid of a Du Pont nitrometer, and in order to obviate the necessity of making a correction for the vapor pressure of acetic acid, citric acid is used instead. They employ cold saturated solutions of citric acid and potassium ferrocyanide, and find that the requisite correction amounts to 1 mm. of mercury for a column of liquid about 12 mm. high. This method for the determination of nitrous acid in the presence of nitric acid is claimed to possess the following advantages over the older methods, in that the volume of gas can be easily read as there is a sharp separation of the mercury from the solution; less mercury is used than in the Lunge method; the method can be applied to concentrated solutions while no strong acids are required. In the method of acid analysis as devised by F. Telle (J. Pharm. Chim. 1906, (6), **23**, 573; abst. Chem. Centr. 1906, **77**, II, 277), 10 cc. of the acid is heated on an oil bath at 130° until red fumes cease to develop. The nitrites present are decomposed by the gradual addition of a saturated solution of ammonium chloride. The sample is then diluted to one liter, and 25 cc. of this solution used for the determination of sulfuric acid. Compare M. Scholtz, Arch. der Pharm. 1906, **243**, 667; abst. Chem. Centr. 1906, **77**, I, 498. F. Telle, J. Pharm. Chim. 1898, (6), **7**, 165; abst. Chem. Centr. 1898, **69**, I, 793.

4. Bull. Soc. Chim. Belg. 1914, **22**, 58; abst. J. S. C. I. 1914, **33**, 834; C. A. 1914, **8**, 2252. For the use of diagrams in chemical calculations see H. Deming, J. Ind. Eng. Chem. 1916, **8**, 264; abst. C. A. 1916, **10**, 1008.

facture. In those methods in which the nitrous and nitric acids are determined together, the nitrous acid then found by permanganate titration, and the nitric acid by difference, oxalic acid which may be present in small quantities as an oxidation product of cellulose would cause high values for nitrous acid and low values to be obtained for nitric acid. Oxalic acid would accumulate in repeatedly used baths, and might render a correction necessary. The oxalic acid may be estimated by neutralizing the acid with ammonia, boiling until nitrous acid is destroyed, and then titrating in the cold with permanganate.

The following method for the analysis of mixed and waste acid has been in use for many years by one of the large explosives companies in the United States, and has been proven trustworthy for waste acids varying greatly in composition and amounts of impurities contained therein.

(a) *Sampling.* A sample of about 125 cc. is taken from the tank after its contents has been thoroughly agitated by means of compressed air to insure that the sample withdrawn is representative. A long glass tube of about 2 meters in length and 2.5 cm. bore, drawn to a tip at the bottom and connected to a rubber tube at the top is used for sampling, the tube being lowered into the acid tank until the acid rises in it to the top. The rubber tube is then pinched at the top, the tube quickly withdrawn, and the acid in the tube transferred to a dry, well-ground glass-stoppered bottle, the tube and bottle being rinsed several times with the acid to be examined before the sample for analysis is taken.

(b) *Total Acidity.* The sample is weighed in a small stoppered weighing bottle, of about 10 cc. capacity, 1 cm. in diameter at the mouth. The bottle being previously weighed from a desiccator, the sample is weighed from a pipette, about 1.2 gm. for spent acid and about 1 gm. for fortifying acid. The sample is transferred as quickly as possible and bottle quickly stoppered. A second weighing gives, by difference, the sample taken.

About 150-175 cc. $N/10$ NaOH are drawn from a burette into a 400 cc. beaker, 10 drops of 1% alcoholic phenolphthalein added.¹ The mouth of the bottle is opened beneath the surface of the liquid in the beaker, the stopper being withdrawn by means

1. Attention is called to the fact that the quantity of phenolphthalein solution used effects the titration to a certain extent and that this amount should be constant both in standardizing the solution and in titrating an acid.

of a specially constructed glass rod. The titration is then continued until nearly all the acid has been neutralized, then the bottle rinsed out with the solution, the gas and air in the bottle being allowed to slowly escape through the alkaline liquid by turning the bottle with the hook. The burette is allowed to stand about 15 minutes, or until the reading is constant after the end-point has been reached. A 225 cc. blue-black bulb burette graduated in 0.1 cc. is used.¹ The total acidity is calculated as sulfuric acid.²

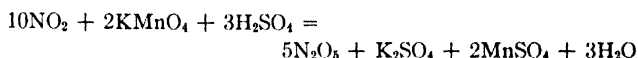
(c) *Total Nitrogen*. About 1.9 gm. spent or 1.2 gm. fortifying acid is weighed in the same kind of container and manner as in (b), quickly poured into a Du Pont nitrometer, in the bulb of which has previously been placed 8–10 cc. of 93% H_2SO_4 , the bottle quickly righted in such a manner as to prevent acid from running down the side, the bottle quickly stoppered and placed in a desiccator. The acid in the nitrometer cup is then quickly washed in with more sulfuric acid, making a total of about 20 cc. H_2SO_4 , and the sample bottle re-weighed as soon as possible. The sampling, transference to nitrometer and final weighing requires some speed and manipulative dexterity, or the results obtained are valueless. The nitrometer is then shaken in the usual manner, and the result read off divided by the weight of the sample taken gives the percentage of total nitrogen. This is converted into percentage of total nitric acid by the factor log. 65303.

(d) *Nitrogen Oxides*. A sample of about 1 gm. for spent or 1.5–2.1 gm. for fortifying acid is weighed as in (b). About 200 cc. distilled water in a beaker is heated to 50°–55°, acidulated with sulfuric acid and colored by a small drop of $N/10 \text{ KMnO}_4$ solution. The sample is then added as in (b), care being taken that the air from the weighing bottle bubbles very slowly through excess of permanganate to prevent loss of oxides. The bulk of

1. Reading corrections should be made for burette calibration at 28° and for temperature; for each degree above or below 28° subtract or add, respectively, 0.01 cc. for each 35 cc. $N/10 \text{ NaOH}$ solution used.

2. The temperature of the NaOH solution is taken by means of two thermometers, one suspended in the carboy of $N/10 \text{ NaOH}$ solution, the other hanging beside the burette. The average of the reading of the two thermometers is taken as the temperature of the solution, except where considerable difference in the temperature of the two solutions has been noted, and the liquid has been in the burette long enough to assume the room temperature. In this case the reading of the thermometer at the side of the burette is taken.

the permanganate is added at once and then gradual additions made as the color fades. A point will be reached where the color fades rapidly, having just before this time persisted for several minutes with the addition of one or two drops of solution. Beyond this point, about one-tenth of the total KMnO_4 is required to complete the reaction. The final reading is taken after the pink color refuses to fade for 10–12 minutes.¹ Calculate from the volume of KMnO_4 used and convert this to equivalent in HNO_3 and H_2SO_4 , based upon the reaction:



Subtract the NO_2 as HNO_3 from the total HNO_3 in (c); difference equals real HNO_3 .

Convert the latter to H_2SO_4 (add log. 89106) and add the NO_2 calculated as H_2SO_4 . This gives HNO_3 plus NO_2 calculated as H_2SO_4 . Deduct this from the total acidity in (b); difference is real sulfuric acid.

(e) *Sulfuric Acid.* This determination is made on 1.8–2 gm. fortifying acid to check the H_2SO_4 by difference. The evaporation takes place in a 2½ inch porcelain crucible lid, nearly flat inside, the sample weighed and transferred to the lid exactly as in the nitrogen determination (c). Evaporate on a steam bath with a good pressure of steam for one hour, then add one cc. water, drop by drop, carefully avoiding any spurting, the lid meanwhile being tilted from side to side so as to cause a flow of the liquid uniformly over the entire surface. Continue evaporation for 30 minutes longer. The crucible and lid is then transferred to a 400 cc. beaker, containing $N/10$ NaOH , and the solution titrated to neutrality by the further addition of caustic solution against phenolphthalein as indicator.

Correction, etc., is made as in (b). Calculate the volume of NaOH used as percentage, H_2SO_4 . This value is slightly lower than the sulfuric acid found by difference, but should check within 0.15%, and is generally closer.

• **Analysis of Mixed Nitrating Acids (English Practice).** The following described methods of analysis as carried out at H. M.

• 1. Corrections for burette and temperature are unnecessary here, as considerable error is required to materially affect the results.

Explosives Plant, Gretna, are employed for all mixed acids with the exception of nitroglycerol spent acid.

The nitrometer method for the determination of total nitrogen acids as herein described is considered the most rapid and at the same time the most accurate method available for the analysis of a mixed acid, but it should be borne in mind that both speed and accuracy are dependent on strict attention to detail.

Strictly normal solutions are used for the titrations so that no corrections are necessary and reference may be made to titration tables. Five figure logarithms are used for the calculations. Three standard solutions are employed: (1) normal sulfuric acid; (2) normal sodium hydroxide; (3) semi-normal potassium permanganate. The solutions are contained in stock bottles on a shelf at a sufficient height to enable the burettes to be filled by gravity. All glass stopcocks are carefully lubricated with vaseline.

Preparation of Samples. The sample as received is thoroughly mixed by shaking and a portion transferred to a small glass stoppered specimen jar for purposes of analysis.

Specific Gravity. A further portion of the thoroughly mixed sample is poured into a hydrometer cylinder and the specific gravity observed by means of a carefully calibrated hydrometer. The hydrometer correction, obtained by reference to the calibration certificate for the hydrometer in use, is applied and the specific gravity finally corrected to 15.5°.

Total Acidity. The total acidity is estimated by titration with normal sodium hydroxide solution and expressed as sulfuric acid. A quantity of acid sufficient to require from 30-40 cc. of N/NaOH for its neutralization, is weighed in an oleum bulb which is then dropped into a titration flask containing 150 cc. of distilled water, and broken by means of a glass rod, care being taken to break up the capillaries of the bulb so that all the acid passes rapidly into solution.

Normal NaOH is run in from a burette at a rate not greater than 30 cc. per minute, but as the indicator used (methyl orange) is readily destroyed by nitrous acid, it is not added until titration is almost complete. During titration the burette jet is rested on the inside of the flask and the alkali allowed to run down the sides; after the addition of the indicator the sides of the flask are washed down with a fine jet of water from a wash bottle and the

titration completed as rapidly as possible, adding the soda a drop at a time.

It is important that only sufficient indicator be added to give a decided color, as an excess impairs the delicacy of the end-point. It is best practice to add two drops of a solution containing 0.05 gram of methyl orange per 100 cc. The end-point is readily observed by comparing the tint of the solution with that of a standard made by passing CO into 200 cc. of distilled water containing two drops of 0.05% methyl orange solution. The end-point being reached, the burette is allowed to drain for two minutes and an observation of the reading taken.

A burette correction obtained by reference to the calibration certificate for the burette in use is applied to the reading, and also a temperature correction to allow for the error due to variation of the temperature of the normal soda in the burette from standard value.

All standard solutions are prepared at 20°, and the burettes are calibrated to deliver Mohr. cc. at the same temperature. For each 50 cc. titration, therefore, 0.015 cc. are subtracted from the burette reading for each degree Centigrade above 20°, or in general work for normal titrations of from 30–40 cubic centimeters, 0.05 cc. are subtracted from the reading for every 5° above and 0.05 cc. added to the reading for every 5° below the standardization temperature (20°).

The approximate weights of the various mixed acids used for the titration so as to give a burette reading of from 30 to 40 cubic centimeters are as follows:

| Mixed Acid | Weight Taken |
|---------------------|---------------|
| N/G Acid Blend | 2.2–2.5 grams |
| N/C Acid Blend | 2.5–2.9 grams |
| R. V. A. Acid Blend | 1.8–2.6 grams |
| N/C Spent Acid | 2.5–3.0 grams |

Total Nitrogen Acids. The total nitrogen acids are estimated by means of the nitrometer (see p. 964–976). A quantity of acid, varying with the nature of the mixed acid being analyzed, is weighed by difference into the cup of the nitrometer to which 2 cc.

H_2SO_4 has previously been added. A Lunge-Rey pipette is used for this purpose and it is given a preliminary washing out with the acid before proceeding with the weighing.

The sample is then run into the nitrometer and the cup thoroughly washed by five successive washings of two cc. of sulfuric acid each, followed by a sixth washing of 5 cc. The acid used for this purpose is pure concentrated nitrogen-free sulfuric acid which has been diluted to a strength of 94.5% acid. In washing out the cup special care is taken to prevent any loss of nitric oxide and to completely wash down the sides of the cup and drain the entire washings into the nitrometer. The approximate weights of the various mixed acids needed to give the desired volume of gas in the nitrometer are as follows:

| Mixed Acid | Weight Taken |
|---------------------|-----------------|
| N/G Acid Blend | 0.65-0.75 grams |
| N/C Acid Blend | 1.25-1.35 grams |
| R. V. A. Acid Blend | 1.5-1.6 grams |
| N/C Spent Acid | 1.5-1.6 grams |

The decomposition is effected by shaking the nitrometer while held in an almost horizontal position; care being taken that the evolved gas is kept under slight suction and that no gas nor acid reaches the rubber tubing of the nitrometer. The tube is shaken for one or two minutes until no more gas is evolved. The two tubes are then placed so that the mercury in the decomposition tube is as much higher than that in the pressure tube as is necessary to compensate for the layer of acid in the latter; 1 mm. of mercury is allowed for every 7 mm. of acid. The nitrometer is allowed to stand for ten minutes in order that the temperature may become equalized and the pressure then exactly adjusted by pouring in a little acid into the cup and cautiously opening the tap. By noting whether the gas is under pressure or suction and by altering the level of the pressure tube accordingly, the pressure of the gas can be exactly compensated with the atmospheric pressure so that when the nitrometer tap is opened the drop of acid in the bore of the tap remains stationary.

The volume of the gas, the barometric pressure and the temperature are then observed; the latter by means of a standardized

thermometer suspended in close proximity to the decomposition bulb of the nitrometer. The barometric reading is corrected accordingly.

It will be observed that the contents of the decomposition bulb after the completion of a determination frequently form a tenacious emulsion which adheres to the sides of the bulb and tube, and makes reading difficult.

This could partly be overcome by washing the bulb and tube down with acid after the decomposition has been effected but the practice is avoided because the acid added after the decomposition will take up an uncertain amount of nitric oxide gas, and is not likely to become saturated. This would interfere with the accuracy of the solubility correction which is finally applied.

The observed volume of the gas is reduced to normal temperature and pressure and the result calculated as percentage of nitric acid (HNO_3). One cubic centimeter of NO gas at normal temperature and pressure corresponds to 2.8144 mgm. HNO_3 , so that the total nitrogen acids expressed as nitric acid is given by the formula

$$v \times 0.0028144 \times 100$$

where v represents the observed volume of the gas and w the weight of mixed acid taken.

A "solubility" correction is applied to allow for the solubility of nitric oxide gas in sulfuric acid. This correction, which is an empirical one, amounts to 1% of the percentage of total nitrogen acids expressed as nitric acids.

If, for example, after all the other corrections have been applied, the nitrometer indicates the presence in a mixed acid of 23.00% of total nitrogen acids, the solubility correction will amount to one per cent. of this value, i. e., 0.23, and the figure returned will be 23.2% of total nitrogen acids.

Nitrous Acid. The nitrous acid content is determined by titration against potassium permanganate solution. Ten cc. of semi-normal potassium permanganate are pipetted into a 500 cc. Erlenmeyer flask containing 200 cc. of distilled water. The acid to be analyzed is then run in slowly from a burette until the color almost vanishes. The end-point aimed at is a faint pink tint

which should remain practically unchanged for about two minutes.

The amount of nitrous acid present is then calculated from the number of cc. of acid used in the titration.

Nitric Acid. The percentage of nitric acid is obtained by subtracting the nitrous acid (expressed as HNO_3) from the total nitrogen acids (also expressed as HNO_3). To this end the percentage of nitrous acid is multiplied by 1.34, which represents the ratio between the equivalent weights of nitric and nitrous acid $\left(\frac{\text{HNO}_3}{\text{HNO}_2} = \frac{63.018}{47.018} = 1.34\right)$ and the value obtained subtracted from the percentage of total nitrogen acids calculated as nitric acid in the manner already indicated.

Sulfuric Acid. The percentage of sulfuric acid present in the sample is obtained by subtracting the value for total nitrogen acids expressed as sulfuric acid from the total acidity expressed in similar terms. For this purpose the percentage of total nitrogen acids expressed as nitric acid (HNO_3) is multiplied by the fraction $\frac{1}{2}$, which represents the ratio between equivalent amounts of sulfuric and nitric acids.

$\left(\frac{\frac{1}{2}\text{H}_2\text{SO}_4}{\text{HNO}_3} = \frac{49.038}{63.018} = \frac{1}{2}\right)$ and the value obtained subtracted from the total acidity calculated as sulfuric acid in the manner already indicated.

Water. The percentage of water present in the sample is obtained by difference, i. e., by subtracting the sum of the sulfuric acid, nitric acid, and nitrous acid percentages from 100.

Summary of Analysis. Sulfuric acid equals total acidity (as H_2SO_4) — total nitric acid (as H_2SO_4). Total nitrogen acids (as HNO_3) obtained directly by analysis. Nitric acid equals total nitric acid (as HNO_3) — HNO_2 as HNO_3 . Nitrous acid is obtained directly by analysis. Water is obtained by difference.

Total Nitrogen Acids. The total nitrogen acids are determined by means of the nitrometer in the manner already described for other mixed acids and the results expressed as nitric acid (HNO_3). The approximate quantity needed to give the desired volume of gas in the nitrometer is from 3.0 to 3.5 grams, and this is weighed in a Lunge-Rey pipette which has previously been washed out with a portion of the sample.

The percentage of nitric acid determined in this way includes

the nitric acid¹ present in the spent acid as nitric esters, etc., but as acid combined in this way is recovered in the denitration process, the method adopted is considered to give a fair indication of the available nitrogen acids.

Sulfuric Acid. The percentage of sulfuric acid is determined by titration of the spent acid with normal sodium hydroxide solution after freeing the sample from total nitrogen acids by evaporation.

About 3.5 grams of the acid are accurately weighed out into a shallow porcelain evaporating dish by means of a Lunge-Rey pipette. A few cc. of water are added and the liquid evaporated in a steam bath for from two to three hours, more water being added about every half hour. To free the liquid from nitric acid quickly it is essential to evaporate down to the smallest possible bulk each time before the addition of a further quantity of water is made. When it is considered that the liquid is completely freed of nitrogen acids, the remaining sulfuric acid is diluted, carefully washed into a titration flask and titrated against normal sodium hydroxide using methyl orange as indicator. As there is little indication to show when all the nitric acid has been driven off, the determinations are always carried out in duplicate. From the number of cc. of normal alkali required for neutralization the percentage of sulfuric acid present in the sample is calculated.

Water. The percentage of water present in the spent acid is obtained by difference, that is, by subtracting the sum of the total nitrogen acids and sulfuric acid from 100.

In the method of calculating for the regeneration of acid baths published by Djeinem,¹ in which empirical formulas are given, the numerous typographical errors materially diminish the value of his work. G. Mowbray² advocates the use of Bessemer steel containers for nitrating acid storage. In handling nitroxylsulfuric acid according to the method of O. Jensen,³ the action of the acid on the iron is said to be prevented by the addition of a small amount of nitric acid (0.5%).

L. White and K. Whitcomb⁴ have described an apparatus

1. Caout. et Gutta-p. 1919, **16**, 9768; abst. C. A. 1919, **13**, 1530.
2. U. S. P. 350498, 1886.
3. U. S. P. 1319586, 1919; abst. J. S. C. I. 1919, **38**, 945-A; C. A. 1920, **11**, 97. Norsk. Hydro-Elektrisk Kvaestofaktieselskab, Norw. P. 23058; E. P. 130966; abst. C. A. 1920, **14**, 97. See also Canadian Explosives, Ltd., Can. P. 165213, 1915. R. Batteg, D. R. P. Aam. B-61729, 1911.
4. U. S. P. 254751, 1882. See also F. Pool, U. S. P. Re-10650, 1885.

for the determination of the degree of nitration of cellular fiber by means of the deflection of a galvanometer, using a cathode and anode on opposite sides of a mixing vessel, the deflection being compared with that of a "standard quality."

P. Pascal and Garnier¹ (see p. 1410) have given in tabular form and also plotted on a triangular graph, the results of an investigation of the densities of nitro-sulfuric mixtures. In the analysis of mixed acids,² T. Chandelon calls attention to the presence of small amounts of oxalic acid formed in nitration which must be taken into account. In the denitration of waste nitrous vitriol according to the process of Farbenfabr. vorm. F. Bayer u. Co.,³ the waste vitriol is concentrated to about 56° Bé. (sp. gr. 1.635), the greater part of the nitric oxide being then removed by passing a stream of air through the hot acid, the last traces being eliminated by treating a stream of the acid with a counter-current of SO₂. The process of concentrating nitric and sulfuric acid of A. Bohre,⁴ and of separating nitric acid from sulfuric acid,⁵ are similar to those already described herein. W. Holmes⁶ has contributed a valuable paper on the freezing points of mixtures of sulfuric and nitric acids.

of U. S. P. 306519. For estimation of nitrogen with nitrometer see E. Beckett, J. C. S. 1920, **117**, 220; abst. C. A. 1920, **14**, 1797. Various acid pumps have been described by W. Hayhurst, J. S. C. I. 1920, **39**, 145-T; abst. C. A. 1920, **14**, 2281. R. Stewart, J. S. C. I. 1920, **39**, 141; abst. C. A. 1920, **14**, 2281. S. Tungay, J. S. C. I. 1920, **39**, 143; abst. C. A. 1920, **14**, 2281. For acid elevator see J. Reavell, J. S. C. I. 1920, **39**, 142-T; abst. C. A. 1920, **14**, 2281. Acid proof coatings for concrete surfaces see E. Berger, Concrete, 1920, **16**, 267; abst. C. A. 1920, **14**, 2404. For construction of acid proof vessels see O. Kausch, Chem. App. 1920, **7**, 49, 66, 76; abst. C. A. 1920, **14**, 2280. A device for distributing liquids about a factory has been patented by H. Crow, E. P. 130940; abst. J. S. C. I. 1920, **39**, 114-T; C. A. 1920, **14**, 2281. For graphic tables for acid calculations and reading device for same, consult M. Hofsass, Zts. ang. Chem. 1919, **32**, I, 319; J. Gasbel. 1920, **62**, 766; C. A. 1920, **14**, 2281. W. Ostwald, Chem. Ztg. 1920, **41**, 241; abst. J. S. C. I. 1920, **39**, 321-A. J. Rudeloff (Zts. Schiess. Spreng. 1907, **2**, 144) and E. Neumann (Spreng. Waffen. Munition, **4**, 4) describe methods for the utilization of spent acids and nitrous gases in the explosive industry.

1. Bull. Soc. Chim. 1919, **25**, 142; abst. J. S. C. I. 1919, **38**, 385-A; C. A. 1919, **13**, 3049.

2. Bull. Soc. Chim. Belg. 1914, **28**, 58; abst. Chem. Zentr. 1914, **85**, I, 1315. Cf.

3. D. R. P. 297902, 1916; abst. J. S. C. I. 1920, **39**, 62-A.

4. U. S. P. 1338418, 1920; abst. J. S. C. I. 1920, **39**, 447-A.

5. C. Kaesmaier, E. P. 2382, 1908; abst. C. A. 1909, **3**, 1330.

6. J. Ind. Eng. Chem. 1920, **12**, 781. M. Allary, J. A. C. S. 1886, **8**, 171. J. A. C. S. 1887, **9**, 38; Bull. Soc. Chim. 1887, **47**, 102. Proc. U. S. Nav. Inst. 1887, **13**, 419; Paint, Oil and Drug Report, 1887, **13**, 9. A. Lerqux,

CHAPTER VIII.

ACID TABLES.

There have been brought together in the thirty-three tables constituting this chapter (Tables I,XXI-CIII) the mathematical data embraced in this and the foregoing section of this volume, it being considered more convenient to locate the tables together than to break up the text by their frequent interspersion.

The series of tables in detail are as follows: Correction for barometer readings for temperature as required in nitrometer work (pp. 1521-1522); density and volume of water (1521-1522); gravity and solubility of sodium nitrate in water (1523-1524); comparison of Baumé and specific gravity readings (1525-1527); specific gravity of oleums (1527-1529) and sulfuric acid (1530-1536), and the influence of temperature on the gravity (1537-1538); thermal properties (1539) and sensible heat (1540) of sulfuric acid and water; hydrometer standardization (1541); conversion of Centigrade to Fahrenheit degrees and conversely (1542-1543); gravity tables for nitric acid (1544-1549); and the weight of 1 cc. moist nitrogen at various temperatures (1549). The series of tables (1550-1565) of correction factors for reducing volume of nitric oxide in cubic centimeters observed on Lunge nitrometer to volume in cubic centimeters to standard conditions, is unusually elaborate, and was first published by the Bureau of Standards. By means of these tables it becomes possible to use a two-bulb nitrometer without calculation for temperature or barometric pressure, by reference to the tables herein.

None of the tables are original with the author, the source being either indicated under the respective table or in the text in connection with the discussion of data to which the table refers,

TABLE LXXI.—REDUCTION OF GAS. VOLUMES TO 0° AND 760 MM.

Volume at 0° and 760 mm. = $\left(\frac{1}{760(1 + 0.00367t)} \right)$ and $(P - p)$

t = observed volume of gas

t = observed temperature of gas in degrees Centigrade

P = observed barometric pressure, corrected, in millimeters

p = tension of aqueous vapor in millimeters

The logarithm of the volume at 0° and 760 mm. is obtained by adding the logs. of $\left(\frac{1}{760(1 + 0.00367t)} \right)$ and $(P - p)$

| Logarithm of 1 760(1+.00367t) | | | Logarithm of 1 760(1+.00367t) | | | Logarithm of 1 760(1+.00367t) | | |
|-------------------------------------|---------|-----------------------------|-------------------------------------|---------|-----------------------------|-------------------------------------|---------|-----------------------------|
| ° C. | | Tension Aqueous Vapor | ° C. | | Tension Aqueous Vapor | ° C. | | Tension Aqueous Vapor |
| | | Mm. | | | Mm. | | | Mm. |
| 0.0 | 3.11919 | 4.60 | 11.8 | 3.10178 | 10.34 | 23.6 | 3.08312 | 21.65 |
| 0.2 | 3.11887 | 4.65 | 12.0 | 3.10047 | 10.48 | 23.8 | 3.08282 | 21.91 |
| 0.4 | 3.11855 | 4.71 | 12.2 | 3.10017 | 10.62 | 24.0 | 3.08253 | 22.18 |
| 0.6 | 3.11824 | 4.78 | 12.4 | 3.09986 | 10.76 | 24.2 | 3.08224 | 22.45 |
| 0.8 | 3.11792 | 4.85 | 12.6 | 3.09956 | 10.90 | 24.4 | 3.08194 | 22.72 |
| 1.0 | 3.11760 | 4.92 | 12.8 | 3.09925 | 11.04 | 24.6 | 3.08165 | 22.99 |
| 1.2 | 3.11728 | 4.99 | 13.0 | 3.09895 | 11.19 | 24.8 | 3.08136 | 23.27 |
| 1.4 | 3.11696 | 5.06 | 13.2 | 3.09864 | 11.33 | 25.0 | 3.08107 | 23.55 |
| 1.6 | 3.11665 | 5.14 | 13.4 | 3.09834 | 11.48 | 25.2 | 3.08078 | 23.83 |
| 1.8 | 3.11633 | 5.21 | 13.6 | 3.09804 | 11.63 | 25.4 | 3.08048 | 24.11 |
| 2.0 | 3.11601 | 5.29 | 13.8 | 3.09773 | 11.78 | 25.6 | 3.08019 | 24.40 |
| 2.2 | 3.11570 | 5.36 | 14.0 | 3.09743 | 11.94 | 25.8 | 3.07990 | 24.69 |
| 2.4 | 3.11538 | 5.44 | 14.2 | 3.09713 | 12.09 | 26.0 | 3.07961 | 24.99 |
| 2.6 | 3.11507 | 5.52 | 14.4 | 3.09682 | 12.25 | 26.2 | 3.07932 | 25.28 |
| 2.8 | 3.11475 | 5.60 | 14.6 | 3.09652 | 12.41 | 26.4 | 3.07903 | 25.58 |
| 3.0 | 3.11443 | 5.68 | 14.8 | 3.09622 | 12.57 | 26.6 | 3.07874 | 25.89 |
| 3.2 | 3.11412 | 5.76 | 15.0 | 3.09592 | 12.73 | 26.8 | 3.07844 | 26.19 |
| 3.4 | 3.11380 | 5.84 | 15.2 | 3.09561 | 12.89 | 27.0 | 3.07816 | 26.50 |
| 3.6 | 3.11349 | 5.92 | 15.4 | 3.09531 | 13.06 | 27.2 | 3.07787 | 26.82 |
| 3.8 | 3.11317 | 6.00 | 15.6 | 3.09501 | 13.23 | 27.4 | 3.07758 | 27.13 |
| 4.0 | 3.11286 | 6.09 | 15.8 | 3.09471 | 13.39 | 27.6 | 3.07729 | 27.45 |
| 4.2 | 3.11255 | 6.17 | 16.0 | 3.09441 | 13.57 | 27.8 | 3.07700 | 27.78 |
| 4.4 | 3.11223 | 6.26 | 16.2 | 3.09411 | 13.74 | 28.0 | 3.07671 | 28.10 |
| 4.6 | 3.11192 | 6.35 | 16.4 | 3.09381 | 13.91 | 28.2 | 3.07642 | 28.43 |
| 4.8 | 3.11160 | 6.44 | 16.6 | 3.09351 | 14.09 | 28.4 | 3.07613 | 28.77 |
| 5.0 | 3.11129 | 6.53 | 16.8 | 3.09321 | 14.27 | 28.6 | 3.07584 | 29.10 |
| 5.2 | 3.11098 | 6.62 | 17.0 | 3.09291 | 14.45 | 28.8 | 3.07555 | 29.44 |
| 5.4 | 3.11067 | 6.71 | 17.2 | 3.09261 | 14.63 | 29.0 | 3.07527 | 29.78 |
| 5.6 | 3.11036 | 6.81 | 17.4 | 3.09231 | 14.82 | 29.2 | 3.07498 | 30.13 |
| 5.8 | 3.11004 | 6.90 | 17.6 | 3.09201 | 15.00 | 29.4 | 3.07469 | 30.48 |
| 6.0 | 3.10973 | 7.00 | 17.8 | 3.09171 | 15.19 | 29.6 | 3.07440 | 30.84 |
| 6.2 | 3.10942 | 7.09 | 18.0 | 3.09141 | 15.38 | 29.8 | 3.07411 | 31.19 |
| 6.4 | 3.10911 | 7.19 | 18.2 | 3.09111 | 15.58 | 30.0 | 3.07383 | 31.56 |
| 6.6 | 3.10880 | 7.29 | 18.4 | 3.09081 | 15.77 | 30.2 | 3.07354 | 31.92 |
| 6.8 | 3.10848 | 7.39 | 18.6 | 3.09051 | 15.97 | 30.4 | 3.07325 | 32.29 |
| 7.0 | 3.10818 | 7.49 | 18.8 | 3.09021 | 16.17 | 30.6 | 3.07297 | 32.66 |
| 7.2 | 3.10786 | 7.60 | 19.0 | 3.08992 | 16.37 | 30.8 | 3.07268 | 33.04 |
| 7.4 | 3.10755 | 7.70 | 19.2 | 3.08962 | 16.57 | 31.0 | 3.07239 | 33.42 |
| 7.6 | 3.10724 | 7.81 | 19.4 | 3.08932 | 16.78 | 31.2 | 3.07211 | 33.80 |
| 7.8 | 3.10693 | 7.91 | 19.6 | 3.08902 | 16.98 | 31.4 | 3.07182 | 34.19 |
| 8.0 | 3.10662 | 8.02 | 19.8 | 3.08873 | 17.19 | 31.6 | 3.07154 | 34.58 |
| 8.2 | 3.10631 | 8.13 | 20.0 | 3.08843 | 17.41 | 31.8 | 3.07125 | 34.97 |
| 8.4 | 3.10600 | 8.24 | 20.2 | 3.08813 | 17.62 | 32.0 | 3.07097 | 35.37 |
| 8.6 | 3.10570 | 8.36 | 20.4 | 3.08783 | 17.84 | 32.2 | 3.07068 | 35.77 |
| 8.8 | 3.10538 | 8.47 | 20.6 | 3.08754 | 18.06 | 32.4 | 3.07039 | 36.18 |
| 9.0 | 3.10508 | 8.58 | 20.8 | 3.08724 | 18.28 | 32.6 | 3.07011 | 36.59 |
| 9.2 | 3.10477 | 8.70 | 21.0 | 3.08695 | 18.50 | 32.8 | 3.06983 | 37.01 |
| 9.4 | 3.10446 | 8.82 | 21.2 | 3.08665 | 18.73 | 33.0 | 3.06954 | 37.43 |
| 9.6 | 3.10415 | 8.94 | 21.4 | 3.08635 | 18.96 | 33.2 | 3.06925 | 37.85 |
| 9.8 | 3.10384 | 9.06 | 21.6 | 3.08606 | 19.19 | 33.4 | 3.06897 | 38.28 |
| 10.0 | 3.10354 | 9.18 | 21.8 | 3.08576 | 19.42 | 33.6 | 3.06869 | 38.71 |
| 10.2 | 3.10323 | 9.30 | 22.0 | 3.08547 | 19.66 | 33.8 | 3.06841 | 39.15 |
| 10.4 | 3.10292 | 9.43 | 22.2 | 3.08517 | 19.90 | 34.0 | 3.06812 | 39.59 |
| 10.6 | 3.10262 | 9.55 | 22.4 | 3.08488 | 20.14 | 34.2 | 3.06784 | 40.03 |
| 10.8 | 3.10231 | 9.68 | 22.6 | 3.08458 | 20.39 | 34.4 | 3.06756 | 40.48 |
| 11.0 | 3.10200 | 9.81 | 22.8 | 3.08429 | 20.63 | 34.6 | 3.06727 | 40.93 |
| 11.2 | 3.10170 | 9.94 | 23.0 | 3.08400 | 20.88 | 34.8 | 3.06699 | 41.38 |
| 11.4 | 3.10139 | 10.07 | 23.2 | 3.08370 | 21.14 | 35.0 | 3.06671 | 41.85 |
| 11.6 | 3.10108 | 10.21 | 23.4 | 3.08341 | 21.39 | | | |

TABLE LXXII.—CORRECTIONS OF BAROMETER READINGS FOR TEMPERATURE

| Barometer Reading, Mm. | GLASS SCALE (BUNSEN) MM. TO BE DEDUCTED | | | | | | | | | |
|------------------------|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1° | 2° | 3° | 4° | 5° | 6° | 7° | 8° | 9° | 10° |
| 700..... | 0.120 | 0.240 | 0.359 | 0.479 | 0.599 | 0.719 | 0.838 | 0.958 | 1.078 | 1.198 |
| 705..... | 0.121 | 0.241 | 0.362 | 0.483 | 0.603 | 0.724 | 0.844 | 0.965 | 1.086 | 1.206 |
| 710..... | 0.121 | 0.243 | 0.364 | 0.486 | 0.607 | 0.729 | 0.850 | 0.972 | 1.093 | 1.215 |
| 715..... | 0.122 | 0.245 | 0.367 | 0.489 | 0.612 | 0.734 | 0.856 | 0.979 | 1.101 | 1.223 |
| 720..... | 0.123 | 0.246 | 0.370 | 0.493 | 0.616 | 0.739 | 0.862 | 0.986 | 1.109 | 1.232 |
| 725..... | 0.124 | 0.248 | 0.372 | 0.496 | 0.620 | 0.744 | 0.868 | 0.992 | 1.116 | 1.240 |
| 730..... | 0.125 | 0.250 | 0.375 | 0.500 | 0.625 | 0.749 | 0.874 | 0.999 | 1.124 | 1.249 |
| 735..... | 0.126 | 0.252 | 0.377 | 0.503 | 0.629 | 0.755 | 0.880 | 1.006 | 1.132 | 1.258 |
| 740..... | 0.127 | 0.253 | 0.380 | 0.506 | 0.633 | 0.760 | 0.886 | 1.013 | 1.140 | 1.266 |
| 745..... | 0.127 | 0.255 | 0.382 | 0.510 | 0.637 | 0.765 | 0.892 | 1.020 | 1.147 | 1.275 |
| 750..... | 0.128 | 0.257 | 0.385 | 0.513 | 0.642 | 0.770 | 0.898 | 1.027 | 1.155 | 1.283 |
| 755..... | 0.129 | 0.258 | 0.388 | 0.517 | 0.646 | 0.775 | 0.904 | 1.033 | 1.163 | 1.292 |
| 760..... | 0.130 | 0.260 | 0.390 | 0.520 | 0.650 | 0.780 | 0.910 | 1.040 | 1.170 | 1.300 |
| 765..... | 0.131 | 0.262 | 0.393 | 0.524 | 0.654 | 0.785 | 0.916 | 1.047 | 1.178 | 1.309 |
| 770..... | 0.132 | 0.264 | 0.395 | 0.527 | 0.659 | 0.790 | 0.922 | 1.054 | 1.186 | 1.317 |
| 775..... | 0.133 | 0.265 | 0.398 | 0.530 | 0.663 | 0.796 | 0.928 | 1.061 | 1.193 | 1.326 |
| 780..... | 0.133 | 0.267 | 0.400 | 0.534 | 0.667 | 0.801 | 0.934 | 1.068 | 1.201 | 1.335 |
| 785..... | 0.134 | 0.269 | 0.403 | 0.537 | 0.672 | 0.806 | 0.940 | 1.075 | 1.209 | 1.343 |
| 790..... | 0.135 | 0.270 | 0.406 | 0.541 | 0.676 | 0.811 | 0.946 | 1.081 | 1.217 | 1.352 |
| 795..... | 0.136 | 0.272 | 0.407 | 0.544 | 0.680 | 0.816 | 0.952 | 1.088 | 1.224 | 1.360 |
| 800..... | 0.137 | 0.273 | 0.411 | 0.548 | 0.684 | 0.821 | 0.958 | 1.095 | 1.232 | 1.369 |

TABLE LXXIII.—DENSITY OF WATER AT 0° TO 36°
WEIGHT IN GRAMS OF ONE CUBIC CENTIMETER OF WATER FREE FROM AIR AT TEMPERATURES OF 0 TO 36 CENTIGRADE BY THE HYDROGEN THERMOMETER—
ACCORDING TO THIESEN, SCHIEHL, AND DIERSCHHORST.

Wiss. Abh. d. Phys.-Techn. Reichsanst. 1900, 3, 68.

| Degrees | Tenths of Degrees | | | | | | | | | |
|---------|-------------------|-----|------|------|------|------|------|------|------|------|
| | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| 0..... | 0.999868 | 874 | 881 | 887 | 893 | 899 | 905 | 911 | 916 | 922 |
| 1..... | | 927 | 932 | 936 | 941 | 945 | 950 | 954 | 957 | 961 |
| 2..... | | 968 | 971 | 974 | 977 | 980 | 982 | 985 | 987 | 989 |
| 3..... | | 992 | 994 | 995 | 996 | 997 | 998 | 999 | 999 | *000 |
| 4..... | 1.000000 | 000 | 000 | *999 | *999 | *998 | *997 | *996 | *995 | *993 |
| 5..... | 0.999992 | 990 | 998 | 986 | 984 | 982 | 979 | 977 | 974 | 971 |
| 6..... | | 986 | 965 | 962 | 958 | 954 | 951 | 947 | 943 | 938 |
| 7..... | | 929 | 925 | 920 | 915 | 910 | 904 | 899 | 893 | 888 |
| 8..... | | 876 | 870 | 864 | 857 | 851 | 844 | 837 | 830 | 823 |
| 9..... | | 808 | 801 | 793 | 785 | 778 | 769 | 761 | 753 | 744 |
| 10..... | | 727 | 718 | 709 | 700 | 691 | 681 | 672 | 662 | 652 |
| 11..... | | 632 | 622 | 612 | 601 | 591 | 580 | 569 | 558 | 547 |
| 12..... | | 525 | 513 | 502 | 490 | 478 | 466 | 454 | 442 | 429 |
| 13..... | | 404 | 391 | 379 | 366 | 353 | 339 | 326 | 312 | 299 |
| 14..... | | 271 | 257 | 243 | 229 | 215 | 200 | 186 | 171 | 156 |
| 15..... | | 126 | 111 | 996 | 081 | 065 | 050 | 034 | 018 | 002 |
| 16..... | 0.998970 | 953 | 937 | 920 | 904 | 887 | 870 | 853 | 836 | 819 |
| 17..... | | 801 | 784 | 766 | 749 | 731 | 713 | 695 | 677 | 659 |
| 18..... | | 622 | 603 | 585 | 566 | 547 | 528 | 509 | 490 | 471 |
| 19..... | | 432 | 412 | 392 | 372 | 352 | 332 | 312 | 292 | 271 |
| 20..... | | 230 | 210 | 189 | 168 | 147 | 126 | 105 | 083 | 062 |
| 21..... | 0.997797 | 019 | *997 | *975 | *953 | *931 | *909 | *887 | *864 | *842 |
| 22..... | | 774 | 751 | 728 | 705 | 682 | 659 | 635 | 612 | 588 |
| 23..... | 0.997797 | 565 | 541 | 517 | 493 | 469 | 445 | 421 | 396 | 372 |
| 24..... | | 323 | 298 | 273 | 248 | 223 | 198 | 173 | 147 | 122 |
| 25..... | | 071 | 045 | 019 | *994 | *968 | *941 | *915 | *889 | *863 |
| 26..... | 0.996810 | 783 | 756 | 730 | 703 | 676 | 648 | 621 | 594 | 567 |
| 27..... | | 539 | 512 | 484 | 456 | 428 | 400 | 372 | 344 | 316 |
| 28..... | | 259 | 231 | 202 | 174 | 145 | 116 | 087 | 058 | 029 |
| 29..... | 0.995971 | 941 | 912 | 882 | 852 | 823 | 793 | 763 | 733 | 703 |
| 30..... | | 673 | 643 | 613 | 582 | 552 | 521 | 491 | 460 | 429 |
| 31..... | | 367 | 336 | 305 | 273 | 242 | 211 | 179 | 148 | 116 |
| 32..... | | 052 | 020 | *988 | *956 | *924 | *892 | *859 | *827 | *794 |
| 33..... | 0.994729 | 696 | 663 | 630 | 597 | 564 | 531 | 498 | 464 | 431 |
| 34..... | | 398 | 364 | 330 | 296 | 263 | 229 | 195 | 161 | 126 |
| 35..... | | 058 | 023 | *989 | *954 | *920 | *885 | *850 | *815 | *780 |

TABLE LXXIV.—DENSITY OF WATER AT 30° TO 102°
WRIGHT IN GRAMS OF ONE CUBIC CENTIMETER OF WATER FREE FROM AIR AT
TEMPERATURES OF 30° TO 102° CENTIGRADE BY THE HYDROGEN
THERMOMETER—According to M. THIRSEN.

Wiss. Abh. d. Phys.—Techn. Reichsanst. 1904, 4, 1^c

| Degrees | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|---------|-----|-----|-----|------|------|------|------|------|------|
| 30..... | 0.99567 | 537 | 505 | 473 | 440 | 406 | 371 | 336 | 299 | 262 |
| 40..... | 0.98807 | 224 | 186 | 147 | 107 | 066 | 025 | *982 | *940 | *896 |
| 50..... | 0.98807 | 762 | 715 | 669 | 621 | 573 | 525 | 475 | 425 | 375 |
| 60..... | 0.97781 | 324 | 272 | 220 | 167 | 113 | 059 | 005 | *950 | *894 |
| 70..... | 0.97781 | 723 | 666 | 607 | 548 | 489 | 429 | 368 | 307 | 245 |
| 80..... | 0.96534 | 183 | 121 | 057 | *094 | *030 | *865 | *800 | *734 | *668 |
| 90..... | 0.96534 | 467 | 399 | 330 | 261 | 192 | 122 | 051 | *981 | *909 |
| 100..... | 0.95838 | 765 | 693 | ... | ... | ... | ... | ... | ... | ... |

TABLE LXXV.—DENSITY OF WATER AT 100° TO 320°
WRIGHT IN GRAMS OF ONE CUBIC CENTIMETER OF WATER AT TEMPERATURES OF
100° TO 320° CENTIGRADE

According to W. RAMSAY, S. YOUNG, J. J. WATERSTON AND G. A. HIRN

| ° C. | Density | ° C. | Density | ° C. | Density | ° C. | Density |
|------|---------|------|---------|------|---------|------|---------|
| 100 | 0.9585 | 160 | 0.8975 | 220 | 0.837 | 280 | 0.75 |
| 110 | 0.9510 | 170 | 0.8973 | 230 | 0.823 | 290 | 0.72 |
| 120 | 0.9434 | 180 | 0.8866 | 240 | 0.809 | 300 | 0.70 |
| 130 | 0.9352 | 190 | 0.8750 | 250 | 0.794 | 310 | 0.68 |
| 140 | 0.9264 | 200 | 0.8628 | 260 | 0.779 | 320 | 0.66 |
| 150 | 0.9173 | 210 | 0.850 | 270 | 0.765 | ... | ... |

To reduce the densities of water free from air to the density of water containing air, add 0.000003 for temperatures of 0 to 14, 0.000002 for temperatures of 15 to 19. For higher temperatures the correction is negligible.

TABLE LXXVI.—VOLUME IN CUBIC CENTIMETERS OF ONE GRAM OF
WATER AT 0° TO 36° CENTIGRADE
BY THE HYDROGEN THERMOMETER—According to THIRSEN, SCHREL, AND
DIERSSELHORST.

Wiss. Abh. d. Phys.—Techn. Reichsanst. 1900, 3, 60

| Degrees | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---------|----------|------|------|------|------|------|------|------|------|------|
| 0..... | 1.000132 | 126 | 119 | 113 | 107 | 101 | 095 | 089 | 084 | 079 |
| 1..... | 073 | 069 | 064 | 059 | 055 | 051 | 047 | 043 | 039 | 035 |
| 2..... | 032 | 029 | 026 | 023 | 020 | 018 | 016 | 013 | 011 | 009 |
| 3..... | 005 | 006 | 005 | 004 | 003 | 002 | 001 | 001 | 000 | 000 |
| 4..... | 000 | 000 | 000 | 001 | 001 | 002 | 003 | 004 | 005 | 007 |
| 5..... | 008 | 010 | 012 | 014 | 016 | 018 | 021 | 023 | 026 | 029 |
| 6..... | 032 | 035 | 039 | 042 | 046 | 050 | 054 | 058 | 062 | 066 |
| 7..... | 071 | 075 | 080 | 085 | 090 | 096 | 101 | 107 | 112 | 118 |
| 8..... | 124 | 130 | 137 | 143 | 149 | 156 | 163 | 170 | 177 | 184 |
| 9..... | 192 | 199 | 207 | 215 | 223 | 231 | 239 | 247 | 256 | 264 |
| 10..... | 273 | 282 | 291 | 300 | 309 | 319 | 328 | 338 | 348 | 358 |
| 11..... | 368 | 378 | 388 | 399 | 409 | 420 | 431 | 442 | 453 | 464 |
| 12..... | 476 | 487 | 499 | 511 | 522 | 534 | 547 | 559 | 571 | 584 |
| 13..... | 596 | 609 | 622 | 635 | 648 | 661 | 675 | 688 | 702 | 715 |
| 14..... | 729 | 743 | 757 | 772 | 786 | 800 | 815 | 830 | 844 | 859 |
| 15..... | 874 | 890 | 905 | 920 | 936 | 951 | 967 | 983 | 999 | *015 |
| 16..... | 1.001031 | 048 | 064 | 081 | 098 | 114 | 131 | 148 | 165 | 183 |
| 17..... | 200 | 218 | 235 | 253 | 271 | 289 | 307 | 325 | 343 | 361 |
| 18..... | 380 | 399 | 417 | 436 | 455 | 474 | 493 | 513 | 532 | 551 |
| 19..... | 571 | 591 | 610 | 630 | 650 | 671 | 691 | 711 | 732 | 752 |
| 20..... | 773 | 794 | 815 | 836 | 857 | 878 | 899 | 921 | 942 | 964 |
| 21..... | 985 | *007 | *029 | *051 | *073 | *096 | *118 | *140 | *162 | *186 |
| 22..... | 1.002208 | 231 | 254 | 277 | 300 | 324 | 347 | 370 | 394 | 418 |
| 23..... | 441 | 465 | 489 | 513 | 538 | 562 | 586 | 611 | 636 | 660 |
| 24..... | 685 | 710 | 735 | 760 | 785 | 810 | 835 | 861 | 886 | 912 |
| 25..... | 938 | 964 | 990 | *016 | *042 | *068 | *094 | *120 | *147 | *174 |
| 26..... | 1.003201 | 227 | 254 | 281 | 308 | 336 | 363 | 390 | 418 | 445 |
| 27..... | 473 | 501 | 529 | 556 | 585 | 613 | 641 | 669 | 698 | 726 |
| 28..... | 755 | 783 | 812 | 841 | 870 | 899 | 928 | 957 | 987 | *016 |
| 29..... | 1.004046 | 075 | 105 | 135 | 165 | 194 | 225 | 255 | 285 | 315 |
| 30..... | 346 | 376 | 407 | 437 | 468 | 499 | 530 | 561 | 592 | 623 |
| 31..... | 655 | 686 | 717 | 748 | 781 | 812 | 844 | 876 | 908 | 940 |
| 32..... | 965 | *037 | *070 | *102 | *135 | *167 | *200 | *233 | *266 | *299 |
| 33..... | 1.005209 | 332 | 365 | 399 | 432 | 465 | 499 | 533 | 566 | 600 |
| 34..... | 634 | 668 | 702 | 736 | 771 | 805 | 839 | 874 | 908 | 943 |
| 35..... | 978 | *013 | *047 | *082 | *118 | *153 | *188 | *223 | *259 | *294 |

TABLE LXXVII.—VOLUME IN CUBIC CENTIMETERS OF ONE GRAM OF WATER AT 30° TO 102° CENTIGRADE

BY THE HYDROGEN THERMOMETER—ACCORDING TO M. THIRSEN
Wiss. Abh. d. Phys.—Techn. Reichsanst. 1904, 4, 1

| Degrees | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|---------|-----|------|------|------|------|------|------|------|------|
| 30..... | 1.00435 | 466 | 497 | 530 | 563 | 598 | 633 | 669 | 706 | 743 |
| 40..... | 782 | 821 | 861 | 901 | 943 | 985 | *028 | *072 | *116 | *162 |
| 50..... | 1.01207 | 254 | 301 | 349 | 398 | 448 | 498 | 548 | 600 | 652 |
| 60..... | 705 | 758 | 813 | 867 | 923 | 979 | *036 | *093 | *151 | *210 |
| 70..... | 1.02270 | 330 | 390 | 452 | 514 | 576 | 639 | 703 | 768 | 833 |
| 80..... | 899 | 965 | *032 | *099 | *168 | *237 | *306 | *376 | *447 | *518 |
| 90..... | 1.03590 | 603 | 736 | 810 | 884 | 959 | *055 | *111 | *188 | *265 |
| 100..... | 1.04343 | 422 | 501 | ... | ... | ... | ... | ... | ... | ... |

To reduce the volumes of water free from air to the volume of water containing air, add 0.000003 for temperatures of 0 to 14, 0.000002 for temperatures of 15 to 19. For higher temperatures the correction is negligible.

TABLE LXXVIII.—VOLUME IN CUBIC CENTIMETERS OF ONE GRAM OF WATER AT 100° TO 320° CENTIGRADE

ACCORDING TO W. RAMSAY, S. YOUNG, J. J. WATERSTON, AND G. A. HURN

| ° C. | Cubic Cent. | ° C. | Cubic Cent. | ° C. | Cubic Cent. | ° C. | Cubic Cent. |
|------|-------------|------|-------------|------|-------------|------|-------------|
| 100 | 1.0433 | 160 | 1.1019 | 220 | 1.195 | 280 | 1.34 |
| 110 | 1.0515 | 170 | 1.1145 | 230 | 1.215 | 290 | 1.38 |
| 120 | 1.0601 | 180 | 1.1279 | 240 | 1.236 | 300 | 1.42 |
| 130 | 1.0693 | 190 | 1.1429 | 250 | 1.259 | 310 | 1.46 |
| 140 | 1.0794 | 200 | 1.1590 | 260 | 1.283 | 320 | 1.51 |
| 150 | 1.0902 | 210 | 1.177 | 270 | 1.308 | ... | ... |

TABLE LXXIX.—SPECIFIC GRAVITY OF SODIUM NITRATE SOLUTIONS AT 20.2° C.

(H. Schuff) Ann. 1858, 107, pp. 59-64

(H. Schiff, calculated by Gerlach, Zts. anal. Chem. 8, 280) from p. 261 of Diet. of Chem. Solubilities, by A. M. Conney, Ph.D.

| Sp. Gr. | % NaNO ₃ | Sp. Gr. | % NaNO ₃ | Sp. Gr. | % NaNO ₃ |
|---------|---------------------|---------|---------------------|---------|---------------------|
| 1.0065 | 1 | .1260 | 18 | .2679 | 35 |
| .0131 | 2 | .1338 | 19 | .2770 | 36 |
| .0197 | 3 | .1418 | 20 | .2863 | 37 |
| .0264 | 4 | .1498 | 21 | .2958 | 38 |
| .0332 | 5 | .1578 | 22 | .3055 | 39 |
| .0399 | 6 | .1659 | 23 | .3155 | 40 |
| .0468 | 7 | .1740 | 24 | .3225 | 41 |
| .0537 | 8 | .1822 | 25 | .3355 | 42 |
| .0606 | 9 | .1904 | 26 | .3456 | 43 |
| .0676 | 10 | .1987 | 27 | .3557 | 44 |
| .0746 | 11 | .2070 | 28 | .3659 | 45 |
| .0817 | 12 | .2154 | 29 | .3761 | 46 |
| .0889 | 13 | .2239 | 30 | .3864 | 47 |
| .0962 | 14 | .2325 | 31 | .3968 | 48 |
| .1035 | 15 | .2412 | 32 | .4074 | 49 |
| .1109 | 16 | .2500 | 33 | .4180 | 50 |
| .1184 | 17 | .2589 | 34 | ... | ... |

TABLE LXXX.—SOLUBILITY OF SODIUM NITRATE IN 100 PARTS H₂O AT t°C.

| t° | Pts. NaNO ₃ | t° | Pts. NaNO ₃ | t° | Pts. NaNO ₃ | t° | Pts. NaNO ₃ |
|----|------------------------|----|------------------------|----|------------------------|-------|------------------------|
| 0 | 72.9 | 31 | 96.0 | 61 | 124 | 91 | 164 |
| 1 | 74.7 | 32 | 96 | 62 | 125 | 92 | 166 |
| 2 | 76.4 | 33 | 97 | 63 | 126 | 93 | 168 |
| 3 | 78.0 | 34 | 98 | 64 | 127 | 94 | 169 |
| 4 | 79.7 | 35 | 99 | 65 | 128 | 95 | 171 |
| 5 | 77.4 | 36 | 100 | 66 | 130 | 96 | 173 |
| 6 | 78.1 | 37 | 100 | 67 | 131 | 97 | 175 |
| 7 | 78.7 | 38 | 101 | 68 | 132 | 98 | 177 |
| 8 | 79.4 | 39 | 102 | 69 | 133 | 99 | 178 |
| 9 | 80.1 | 40 | 102 | 70 | 134 | 100 | 180 |
| 10 | 80.8 | 41 | 103 | 71 | 136 | 101 | 182 |
| 11 | 81.4 | 42 | 104 | 72 | 137 | 102 | 184 |
| 12 | 82.0 | 43 | 105 | 73 | 138 | 103 | 186 |
| 13 | 82.7 | 44 | 106 | 74 | 139 | 104 | 188 |
| 14 | 83.4 | 45 | 107 | 75 | 140 | 105 | 190 |
| 15 | 84.0 | 46 | 108 | 76 | 142 | 106 | 192 |
| 16 | 84.7 | 47 | 109 | 77 | 143 | 107 | 194 |
| 17 | 85.4 | 48 | 110 | 78 | 145 | 108 | 196 |
| 18 | 86.1 | 49 | 111 | 79 | 146 | 109 | 198 |
| 19 | 86.8 | 50 | 112 | 80 | 148 | 110 | 200 |
| 20 | 87.5 | 51 | 113 | 81 | 149 | 111 | 202 |
| 21 | 88.3 | 52 | 114 | 82 | 151 | 112 | 204 |
| 22 | 89.0 | 53 | 115 | 83 | 152 | 113 | 207 |
| 23 | 89.7 | 54 | 116 | 84 | 153 | 114 | 209 |
| 24 | 90.3 | 55 | 117 | 85 | 155 | 115 | 211 |
| 25 | 91.0 | 56 | 118 | 86 | 156 | 116 | 213 |
| 26 | 91.8 | 57 | 119 | 87 | 158 | 117 | 215 |
| 27 | 92.5 | 58 | 120 | 88 | 159 | 117.5 | 216.4 |
| 28 | 93.2 | 59 | 121 | 89 | 161 | | |
| 29 | 94.0 | 60 | 122 | 90 | 162 | | |
| 30 | 94.9 | | | | | | |

(Mulder, Scheik, Verhandel, 1864, 83.)

Sat. solution at b.-pt. contains 216.4 pts. NaNO₃ (Mulder); 218.5 pts. NaNO₃ (Marx); 213.4 pts. NaNO₃ (Maumene); 211.4 pts. NaNO₃ (Nordenskjöld); 224.8 pts. NaNO₃ (Legrand); 150 pts. NaNO₃ (Griffiths).

Taken from "A Dictionary of Chemical Solubilities," by A. M. Comey, page 261.

TABLE LXXXI

Another table, for the temperature 15° C., is given by Scott (*Pharm. Soc. J. and Trans.* i. p. 217):

| Per cent. SO ₂ | Specific Gravity | Per cent. SO ₂ | Specific Gravity |
|---------------------------|------------------|---------------------------|------------------|
| 0.5 | 1.0028 | 5.5 | 1.0302 |
| 1.0 | 1.0056 | 6.0 | 1.0328 |
| 1.5 | 1.0085 | 6.5 | 1.0353 |
| 2.0 | 1.0113 | 7.0 | 1.0377 |
| 2.5 | 1.0141 | 7.5 | 1.0401 |
| 3.0 | 1.0168 | 8.0 | 1.0426 |
| 3.5 | 1.0194 | 8.5 | 1.0450 |
| 4.0 | 1.0221 | 9.0 | 1.0474 |
| 4.5 | 1.0248 | 9.5 | 1.0497 |
| 5.0 | 1.0275 | 10.0 | 1.0520 |

Much higher are the figures given by Pellet (*J. Soc. Chem. Ind.* 1902, p. 171):

| Per cent. SO ₂ in 100 H ₂ O. | 1 | 2 | 3 | 4 | 5 | 6 |
|--|--------|-------|--------|-------|--------|-------|
| Sp. gr. at 15° to 17° C..... | 1.0075 | 1.015 | 1.0225 | 1.030 | 1.0375 | 1.045 |

TABLE LXXXII

From Bunsen and Schönfeld's determinations, HARRIS (*Chem. Zeit.* 1905, p. 136) calculated the following table (for normal atmospheric pressure):

| Temp., degrees | 1 Lit. Water Dissolves Lit. SO ₂ | 1 Lit. Water Dissolves Grammes SO ₂ | 1 Lit. Saturated Aqueous Solution Contains Lit. SO ₂ | Specific Gravity of Aqueous Solution | Per cent. SO ₂ by Weight in the Aqueous Solution |
|-------------------|---|--|--|---|--|
| 0 | 79.8 | 228.3 | 68.89 | 1.0609 | 18.58 |
| 5 | 57.5 | 193.1 | 59.82 | 1.059 | 16.19 |
| 10 | 56.6 | 191.9 | 51.38 | 1.0547 | 13.93 |
| 15 | 47.3 | 135.3 | 43.56 | 1.042 | 11.82 |
| 20 | 39.4 | 112.7 | 36.21 | 1.0239 | 10.12 |

TABLE LXXXIII.—EQUIVALENT OF DEGREES BAUMÉ (AMERICAN STANDARD) AND SPECIFIC GRAVITY AT 60° F.

| Degrees Baumé = 145 — 145 Sp. Gr. | | | | For Liquids Heavier than Water | | | |
|--------------------------------------|------------------|---------------|------------------|--------------------------------|------------------|---------------|------------------|
| Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity |
| 0.0 | 1.0000 | 7.0 | 1.0507 | 14.0 | 1.1069 | 21.0 | 1.1694 |
| .1 | 1.0007 | .1 | 1.0515 | .1 | 1.1077 | .1 | 1.1703 |
| .2 | 1.0014 | .2 | 1.0522 | .2 | 1.1086 | .2 | 1.1712 |
| .3 | 1.0021 | .3 | 1.0530 | .3 | 1.1094 | .3 | 1.1722 |
| .4 | 1.0028 | .4 | 1.0538 | .4 | 1.1103 | .4 | 1.1731 |
| .5 | 1.0035 | .5 | 1.0545 | .5 | 1.1111 | .5 | 1.1741 |
| .6 | 1.0042 | .6 | 1.0553 | .6 | 1.1120 | .6 | 1.1750 |
| .7 | 1.0049 | .7 | 1.0561 | .7 | 1.1128 | .7 | 1.1760 |
| .8 | 1.0055 | .8 | 1.0569 | .8 | 1.1137 | .8 | 1.1769 |
| .9 | 1.0062 | .9 | 1.0576 | .9 | 1.1145 | .9 | 1.1779 |
| 1.0 | 1.0069 | 8.0 | 1.0584 | 15.0 | 1.1154 | 22.0 | 1.1789 |
| .1 | 1.0076 | .1 | 1.0592 | .1 | 1.1162 | .1 | 1.1798 |
| .2 | 1.0083 | .2 | 1.0599 | .2 | 1.1171 | .2 | 1.1808 |
| .3 | 1.0090 | .3 | 1.0607 | .3 | 1.1180 | .3 | 1.1817 |
| .4 | 1.0097 | .4 | 1.0615 | .4 | 1.1188 | .4 | 1.1827 |
| .5 | 1.0105 | .5 | 1.0623 | .5 | 1.1197 | .5 | 1.1837 |
| .6 | 1.0112 | .6 | 1.0630 | .6 | 1.1206 | .6 | 1.1846 |
| .7 | 1.0119 | .7 | 1.0638 | .7 | 1.1214 | .7 | 1.1856 |
| .8 | 1.0126 | .8 | 1.0646 | .8 | 1.1223 | .8 | 1.1865 |
| .9 | 1.0133 | .9 | 1.0654 | .9 | 1.1232 | .9 | 1.1876 |
| 1.0 | 1.0140 | 9.0 | 1.0662 | 16.0 | 1.1240 | 23.0 | 1.1885 |
| .1 | 1.0147 | .1 | 1.0670 | .1 | 1.1249 | .1 | 1.1895 |
| .2 | 1.0154 | .2 | 1.0677 | .2 | 1.1258 | .2 | 1.1905 |
| .3 | 1.0161 | .3 | 1.0685 | .3 | 1.1267 | .3 | 1.1915 |
| .4 | 1.0168 | .4 | 1.0693 | .4 | 1.1275 | .4 | 1.1924 |
| .5 | 1.0175 | .5 | 1.0701 | .5 | 1.1284 | .5 | 1.1934 |
| .6 | 1.0183 | .6 | 1.0709 | .6 | 1.1293 | .6 | 1.1944 |
| .7 | 1.0190 | .7 | 1.0717 | .7 | 1.1302 | .7 | 1.1954 |
| .8 | 1.0197 | .8 | 1.0725 | .8 | 1.1310 | .8 | 1.1964 |
| .9 | 1.0204 | .9 | 1.0733 | .9 | 1.1319 | .9 | 1.1974 |
| 1.0 | 1.0211 | 10.0 | 1.0741 | 17.0 | 1.1328 | 24.0 | 1.1983 |
| .1 | 1.0218 | .1 | 1.0749 | .1 | 1.1337 | .1 | 1.1993 |
| .2 | 1.0226 | .2 | 1.0757 | .2 | 1.1346 | .2 | 1.2003 |
| .3 | 1.0233 | .3 | 1.0765 | .3 | 1.1355 | .3 | 1.2013 |
| .4 | 1.0240 | .4 | 1.0773 | .4 | 1.1364 | .4 | 1.2023 |
| .5 | 1.0247 | .5 | 1.0781 | .5 | 1.1373 | .5 | 1.2033 |
| .6 | 1.0255 | .6 | 1.0789 | .6 | 1.1381 | .6 | 1.2043 |
| .7 | 1.0262 | .7 | 1.0797 | .7 | 1.1390 | .7 | 1.2053 |
| .8 | 1.0269 | .8 | 1.0805 | .8 | 1.1399 | .8 | 1.2063 |
| .9 | 1.0276 | .9 | 1.0813 | .9 | 1.1408 | .9 | 1.2073 |
| 1.0 | 1.0284 | 11.0 | 1.0821 | 18.0 | 1.1417 | 25.0 | 1.2083 |
| .1 | 1.0291 | .1 | 1.0829 | .1 | 1.1426 | .1 | 1.2093 |
| .2 | 1.0298 | .2 | 1.0837 | .2 | 1.1435 | .2 | 1.2104 |
| .3 | 1.0306 | .3 | 1.0845 | .3 | 1.1444 | .3 | 1.2114 |
| .4 | 1.0313 | .4 | 1.0853 | .4 | 1.1453 | .4 | 1.2124 |
| .5 | 1.0320 | .5 | 1.0861 | .5 | 1.1462 | .5 | 1.2134 |
| .6 | 1.0328 | .6 | 1.0870 | .6 | 1.1472 | .6 | 1.2144 |
| .7 | 1.0335 | .7 | 1.0878 | .7 | 1.1481 | .7 | 1.2154 |
| .8 | 1.0342 | .8 | 1.0886 | .8 | 1.1490 | .8 | 1.2164 |
| .9 | 1.0350 | .9 | 1.0894 | .9 | 1.1499 | .9 | 1.2175 |
| 1.0 | 1.0357 | 12.0 | 1.0902 | 19.0 | 1.1508 | 26.0 | 1.2185 |
| .1 | 1.0365 | .1 | 1.0910 | .1 | 1.1517 | .1 | 1.2195 |
| .2 | 1.0372 | .2 | 1.0919 | .2 | 1.1526 | .2 | 1.2205 |
| .3 | 1.0379 | .3 | 1.0927 | .3 | 1.1535 | .3 | 1.2216 |
| .4 | 1.0387 | .4 | 1.0935 | .4 | 1.1545 | .4 | 1.2226 |
| .5 | 1.0394 | .5 | 1.0943 | .5 | 1.1554 | .5 | 1.2236 |
| .6 | 1.0402 | .6 | 1.0952 | .6 | 1.1563 | .6 | 1.2247 |
| .7 | 1.0409 | .7 | 1.0960 | .7 | 1.1572 | .7 | 1.2257 |
| .8 | 1.0417 | .8 | 1.0968 | .8 | 1.1581 | .8 | 1.2267 |
| .9 | 1.0424 | .9 | 1.0977 | .9 | 1.1591 | .9 | 1.2278 |
| 1.0 | 1.0432 | 13.0 | 1.0985 | 20.0 | 1.1600 | 27.0 | 1.2288 |
| .1 | 1.0439 | .1 | 1.0993 | .1 | 1.1609 | .1 | 1.2299 |
| .2 | 1.0447 | .2 | 1.1002 | .2 | 1.1619 | .2 | 1.2309 |
| .3 | 1.0454 | .3 | 1.1010 | .3 | 1.1628 | .3 | 1.2319 |
| .4 | 1.0462 | .4 | 1.1018 | .4 | 1.1637 | .4 | 1.2330 |
| .5 | 1.0469 | .5 | 1.1027 | .5 | 1.1647 | .5 | 1.2340 |
| .6 | 1.0477 | .6 | 1.1035 | .6 | 1.1656 | .6 | 1.2351 |
| .7 | 1.0484 | .7 | 1.1043 | .7 | 1.1665 | .7 | 1.2361 |
| .8 | 1.0492 | .8 | 1.1052 | .8 | 1.1675 | .8 | 1.2372 |
| .9 | 1.0500 | .9 | 1.1060 | .9 | 1.1684 | .9 | 1.2383 |

TABLE LXXXIII. (Continued)

| Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity |
|------------------|---------------------|------------------|---------------------|------------------|---------------------|------------------|---------------------|
| 28.0 | 1.2393 | .3 | 1.3218 | .6 | 1.4160 | .9 | 1.5247 |
| .1 | 1.2404 | .4 | 1.3230 | .7 | 1.4174 | 50.0 | 1.5263 |
| .2 | 1.2414 | .5 | 1.3242 | .8 | 1.4188 | .1 | 1.5279 |
| .3 | 1.2425 | .6 | 1.3254 | .9 | 1.4202 | .2 | 1.5295 |
| .4 | 1.2436 | .7 | 1.3266 | 43.0 | 1.4216 | .3 | 1.5312 |
| .5 | 1.2446 | .8 | 1.3278 | .1 | 1.4330 | .4 | 1.5328 |
| .6 | 1.2457 | .9 | 1.3291 | .2 | 1.4244 | .5 | 1.5344 |
| .7 | 1.2468 | 36.0 | 1.3303 | .3 | 1.4258 | .6 | 1.5360 |
| .8 | 1.2478 | .1 | 1.3315 | .4 | 1.4272 | .7 | 1.5376 |
| .9 | 1.2489 | .2 | 1.3327 | .5 | 1.4286 | .8 | 1.5393 |
| 29.0 | 1.2500 | .3 | 1.3329 | .6 | 1.4300 | .9 | 1.5409 |
| .1 | 1.2511 | .4 | 1.3352 | .7 | 1.4314 | 51.0 | 1.5426 |
| .2 | 1.2522 | .5 | 1.3364 | .8 | 1.4328 | .1 | 1.5442 |
| .3 | 1.2532 | .6 | 1.3376 | .9 | 1.4342 | .2 | 1.5458 |
| .4 | 1.2543 | .7 | 1.3389 | 44.0 | 1.4356 | .3 | 1.5475 |
| .5 | 1.2554 | .8 | 1.3401 | .1 | 1.4371 | .4 | 1.5491 |
| .6 | 1.2565 | .9 | 1.3414 | .2 | 1.4385 | .5 | 1.5508 |
| .7 | 1.2576 | 37.0 | 1.3426 | .3 | 1.4399 | .6 | 1.5525 |
| .8 | 1.2587 | .1 | 1.3438 | .4 | 1.4414 | .7 | 1.5541 |
| .9 | 1.2598 | .2 | 1.3451 | .5 | 1.4428 | .8 | 1.5558 |
| 30.0 | 1.2609 | .3 | 1.3463 | .6 | 1.4442 | .9 | 1.5575 |
| .1 | 1.2620 | .4 | 1.3476 | .7 | 1.4457 | 52.0 | 1.5591 |
| .2 | 1.2631 | .5 | 1.3488 | .8 | 1.4471 | .1 | 1.5608 |
| .3 | 1.2642 | .6 | 1.3501 | .9 | 1.4486 | .2 | 1.5625 |
| .4 | 1.2653 | .7 | 1.3514 | 45.0 | 1.4500 | .3 | 1.5642 |
| .5 | 1.2664 | .8 | 1.3526 | .1 | 1.4515 | .4 | 1.5659 |
| .6 | 1.2675 | .9 | 1.3539 | .2 | 1.4529 | .5 | 1.5676 |
| .7 | 1.2686 | 38.0 | 1.3551 | .3 | 1.4544 | .6 | 1.5693 |
| .8 | 1.2697 | .1 | 1.3564 | .4 | 1.4558 | .7 | 1.5710 |
| .9 | 1.2708 | .2 | 1.3577 | .5 | 1.4573 | .8 | 1.5727 |
| 31.0 | 1.2719 | .3 | 1.3590 | .6 | 1.4588 | .9 | 1.5744 |
| .1 | 1.2730 | .4 | 1.3602 | .7 | 1.4602 | 53.0 | 1.5761 |
| .2 | 1.2742 | .5 | 1.3615 | .8 | 1.4617 | .1 | 1.5778 |
| .3 | 1.2753 | .6 | 1.3628 | .9 | 1.4632 | .2 | 1.5795 |
| .4 | 1.2764 | .7 | 1.3641 | 46.0 | 1.4646 | .3 | 1.5812 |
| .5 | 1.2775 | .8 | 1.3653 | .1 | 1.4661 | .4 | 1.5830 |
| .6 | 1.2787 | .9 | 1.3666 | .2 | 1.4676 | .5 | 1.5847 |
| .7 | 1.2798 | 39.0 | 1.3679 | .3 | 1.4691 | .6 | 1.5864 |
| .8 | 1.2809 | .1 | 1.3692 | .4 | 1.4706 | .7 | 1.5882 |
| .9 | 1.2821 | .2 | 1.3705 | .5 | 1.4721 | .8 | 1.5899 |
| 32.0 | 1.2832 | .3 | 1.3718 | .6 | 1.4736 | .9 | 1.5917 |
| .1 | 1.2843 | .4 | 1.3731 | .7 | 1.4751 | 54.0 | 1.5934 |
| .2 | 1.2855 | .5 | 1.3744 | .8 | 1.4766 | .1 | 1.5952 |
| .3 | 1.2866 | .6 | 1.3757 | .9 | 1.4781 | .2 | 1.5969 |
| .4 | 1.2877 | .7 | 1.3770 | 47.0 | 1.4796 | .3 | 1.5987 |
| .5 | 1.2889 | .8 | 1.3783 | .1 | 1.4811 | .4 | 1.6004 |
| .6 | 1.2900 | .9 | 1.3796 | .2 | 1.4826 | .5 | 1.6022 |
| .7 | 1.2912 | 40.0 | 1.3810 | .3 | 1.4841 | .6 | 1.6040 |
| .8 | 1.2923 | .1 | 1.3823 | .4 | 1.4857 | .7 | 1.6058 |
| .9 | 1.2935 | .2 | 1.3836 | .5 | 1.4872 | .8 | 1.6075 |
| 33.0 | 1.2946 | .3 | 1.3849 | .6 | 1.4887 | .9 | 1.6093 |
| .1 | 1.2958 | .4 | 1.3862 | .7 | 1.4902 | 55.0 | 1.6111 |
| .2 | 1.2970 | .5 | 1.3876 | .8 | 1.4918 | .1 | 1.6129 |
| .3 | 1.2981 | .6 | 1.3889 | .9 | 1.4933 | .2 | 1.6147 |
| .4 | 1.2993 | .7 | 1.3902 | 48.0 | 1.4948 | .3 | 1.6165 |
| .5 | 1.3004 | .8 | 1.3916 | .1 | 1.4964 | .4 | 1.6183 |
| .6 | 1.3016 | .9 | 1.3929 | .2 | 1.4979 | .5 | 1.6201 |
| .7 | 1.3028 | 41.0 | 1.3942 | .3 | 1.4995 | .6 | 1.6219 |
| .8 | 1.3040 | .1 | 1.3956 | .4 | 1.5010 | .7 | 1.6237 |
| .9 | 1.3051 | .2 | 1.3969 | .5 | 1.5026 | .8 | 1.6256 |
| 34.0 | 1.3063 | .3 | 1.3983 | .6 | 1.5041 | .9 | 1.6274 |
| .1 | 1.3075 | .4 | 1.3996 | .7 | 1.5057 | 56.0 | 1.6292 |
| .2 | 1.3087 | .5 | 1.4010 | .8 | 1.5073 | .1 | 1.6310 |
| .3 | 1.3098 | .6 | 1.4023 | .9 | 1.5088 | .2 | 1.6329 |
| .4 | 1.3110 | .7 | 1.4037 | 49.0 | 1.5104 | .3 | 1.6347 |
| .5 | 1.3122 | .8 | 1.4050 | .1 | 1.5120 | .4 | 1.6366 |
| .6 | 1.3134 | .9 | 1.4064 | .2 | 1.5136 | .5 | 1.6384 |
| .7 | 1.3146 | 42.0 | 1.4078 | .3 | 1.5152 | .6 | 1.6403 |
| .8 | 1.3158 | .1 | 1.4091 | .4 | 1.5167 | .7 | 1.6421 |
| .9 | 1.3170 | .2 | 1.4105 | .5 | 1.5183 | .8 | 1.6440 |
| 35.0 | 1.3182 | .3 | 1.4119 | .6 | 1.5199 | .9 | 1.6459 |
| .1 | 1.3194 | .4 | 1.4133 | .7 | 1.5215 | 57.0 | 1.6477 |
| .2 | 1.3206 | .5 | 1.4146 | .8 | 1.5231 | .1 | 1.6496 |

TABLE LXXXIII. (Concluded)

| Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity | Degrees Baumé | Specific Gravity |
|------------------|---------------------|------------------|---------------------|------------------|---------------------|------------------|---------------------|
| .2 | 1.6515 | .5 | 1.7160 | .8 | 1.7857 | 67.0 | 1.8590 |
| .3 | 1.6534 | .6 | 1.7180 | .9 | 1.7879 | .1 | 1.8614 |
| .4 | 1.6553 | .7 | 1.7200 | 64.0 | 1.7901 | .2 | 1.8638 |
| .5 | 1.6571 | .8 | 1.7221 | .1 | 1.7923 | .3 | 1.8662 |
| .6 | 1.6590 | .9 | 1.7241 | .2 | 1.7946 | .4 | 1.8686 |
| .7 | 1.6609 | 61.0 | 1.7262 | .3 | 1.7968 | .5 | 1.8710 |
| .8 | 1.6628 | .1 | 1.7282 | .4 | 1.7990 | .6 | 1.8734 |
| .9 | 1.6648 | .2 | 1.7303 | .5 | 1.8012 | .7 | 1.8758 |
| 58.0 | 1.6667 | .3 | 1.7324 | .6 | 1.8035 | .8 | 1.8782 |
| .1 | 1.6686 | .4 | 1.7344 | .7 | 1.8057 | .9 | 1.8807 |
| .2 | 1.6705 | .5 | 1.7365 | .8 | 1.8080 | 68.0 | 1.8831 |
| .3 | 1.6724 | .6 | 1.7386 | .9 | 1.8102 | .1 | 1.8856 |
| .4 | 1.6744 | .7 | 1.7407 | 65.0 | 1.8125 | .2 | 1.8880 |
| .5 | 1.6763 | .8 | 1.7428 | .1 | 1.8148 | .3 | 1.8905 |
| .6 | 1.6782 | .9 | 1.7449 | .2 | 1.8170 | .4 | 1.8930 |
| .7 | 1.6802 | 62.0 | 1.7470 | .3 | 1.8193 | .5 | 1.8954 |
| .8 | 1.6821 | .1 | 1.7491 | .4 | 1.8216 | .6 | 1.8979 |
| .9 | 1.6841 | .2 | 1.7512 | .5 | 1.8239 | .7 | 1.9004 |
| 59.0 | 1.6860 | .3 | 1.7533 | .6 | 1.8262 | .8 | 1.9029 |
| .1 | 1.6880 | .4 | 1.7554 | .7 | 1.8285 | .9 | 1.9054 |
| .2 | 1.6900 | .5 | 1.7576 | .8 | 1.8308 | 69.0 | 1.9079 |
| .3 | 1.6919 | .6 | 1.7597 | .9 | 1.8331 | .1 | 1.9104 |
| .4 | 1.6939 | .7 | 1.7618 | 66.0 | 1.8354 | .2 | 1.9129 |
| .5 | 1.6959 | .8 | 1.7640 | .1 | 1.8378 | .3 | 1.9154 |
| .6 | 1.6979 | .9 | 1.7661 | .2 | 1.8401 | .4 | 1.9180 |
| .7 | 1.6999 | 63.0 | 1.7683 | .3 | 1.8424 | .5 | 1.9205 |
| .8 | 1.7019 | .1 | 1.7705 | .4 | 1.8448 | .6 | 1.9231 |
| .9 | 1.7039 | .2 | 1.7726 | .5 | 1.8471 | .7 | 1.9256 |
| 60.0 | 1.7059 | .3 | 1.7748 | .6 | 1.8495 | .8 | 1.9282 |
| .1 | 1.7079 | .4 | 1.7770 | .7 | 1.8519 | .9 | 1.9308 |
| .2 | 1.7099 | .5 | 1.7791 | .8 | 1.8542 | 70.0 | 1.9333 |
| .3 | 1.7119 | .6 | 1.7813 | .9 | 1.8566 | | |
| .4 | 1.7139 | .7 | 1.7835 | | | | |

TABLE LXXXIV.—SPECIFIC GRAVITY OF FUMING SULFURIC ACID AT 35° C.
(R. Knietzsch) (Ber. 1901, 34, 4101)

| Sp. Gr. | Total SO ₃ % | Free SO ₃ % | Sp. Gr. | Total SO ₃ % | Free SO ₃ % |
|---------|----------------------------|---------------------------|---------|----------------------------|---------------------------|
| 1.8186 | 81.63 | 0 | 1.9749 | 91.18 | 52 |
| 270 | 81.99 | 2 | 760 | 91.55 | 54 |
| 360 | 82.36 | 4 | 772 | 91.91 | 56 |
| 425 | 82.73 | 6 | 754 | 92.28 | 58 |
| 498 | 83.09 | 8 | 738 | 92.65 | 60 |
| 565 | 83.46 | 10 | 709 | 93.02 | 62 |
| 627 | 83.82 | 12 | 672 | 93.38 | 64 |
| 692 | 84.20 | 14 | 636 | 93.75 | 66 |
| 756 | 84.56 | 16 | 600 | 94.11 | 68 |
| 830 | 84.92 | 18 | 564 | 94.48 | 70 |
| 918 | 85.30 | 20 | 502 | 94.85 | 72 |
| 9020 | 85.66 | 22 | 442 | 95.21 | 74 |
| 092 | 86.03 | 24 | 379 | 95.58 | 76 |
| 158 | 86.40 | 26 | 315 | 95.95 | 78 |
| 220 | 86.76 | 28 | 251 | 96.32 | 80 |
| 280 | 87.14 | 30 | 183 | 96.69 | 82 |
| 338 | 87.50 | 32 | 115 | 97.05 | 84 |
| 405 | 87.87 | 34 | 046 | 97.42 | 86 |
| 474 | 88.24 | 36 | 1.8980 | 97.78 | 88 |
| 534 | 88.60 | 38 | 888 | 98.16 | 90 |
| 584 | 88.97 | 40 | 800 | 98.53 | 92 |
| 612 | 89.33 | 42 | 712 | 98.90 | 94 |
| 643 | 89.70 | 44 | 605 | 99.26 | 96 |
| 672 | 90.07 | 46 | 488 | 99.63 | 98 |
| 702 | 90.44 | 48 | 370 | 100.00 | 100 |
| 733 | 90.81 | 50 | | | |

TABLE LXXXV.—FUMING SULFURIC ACID

FREE SO₃, TOTAL SO₃ AND EQUIVALENT VALUES IN TERMS OF 100%, 98% AND 93.19% H₂SO₄
(H. BISHOP)

| Actual Composition | | Equivalents | | | | Actual Composition | | Equivalents | | | |
|----------------------|--|-----------------------|-------------------------------------|------------------------------------|--|--------------------------------|--|-----------------------|-------------------------------------|------------------------------------|--|
| Free SO ₃ | Per cent. H ₂ SO ₄ | Total SO ₃ | 100% H ₂ SO ₄ | 98% H ₂ SO ₄ | H ₂ SO ₄ 93.19% 66° B _e . | Per cent. Free SO ₃ | Per cent. H ₂ SO ₄ | Total SO ₃ | 100% H ₂ SO ₄ | 98% H ₂ SO ₄ | H ₂ SO ₄ 93.19% 66° B _e . |
| 100 | | 81.63 | 100.00 | 102.04 | 107.31 | 50 | 50 | 90.82 | 111.25 | 113.52 | 119.68 |
| 99 | | 81.82 | 100.23 | 102.27 | 107.55 | 51 | 49 | 91.00 | 111.48 | 113.75 | 119.82 |
| 98 | | 82.07 | 100.45 | 102.50 | 107.79 | 52 | 48 | 91.18 | 111.70 | 113.98 | 119.86 |
| 97 | | 82.18 | 100.67 | 102.73 | 108.03 | 53 | 47 | 91.37 | 111.93 | 114.21 | 120.11 |
| 96 | | 82.37 | 100.90 | 102.96 | 108.28 | 54 | 46 | 91.55 | 112.15 | 114.44 | 120.35 |
| 95 | | 82.55 | 101.13 | 103.19 | 108.52 | 55 | 45 | 91.73 | 112.37 | 114.67 | 120.59 |
| 94 | | 82.73 | 101.35 | 103.42 | 108.76 | 56 | 44 | 91.92 | 112.60 | 114.90 | 120.83 |
| 93 | | 82.92 | 101.58 | 103.65 | 109.00 | 57 | 43 | 92.10 | 112.82 | 115.13 | 121.07 |
| 92 | | 83.10 | 101.80 | 103.88 | 109.24 | 58 | 42 | 92.29 | 113.05 | 115.36 | 121.31 |
| 91 | | 83.29 | 102.03 | 104.11 | 109.48 | 59 | 41 | 92.47 | 113.28 | 115.59 | 121.55 |
| 90 | | 83.47 | 102.25 | 104.34 | 109.72 | 60 | 40 | 92.65 | 113.50 | 115.82 | 121.79 |
| 89 | | 83.65 | 102.47 | 104.57 | 109.96 | 61 | 39 | 92.84 | 113.73 | 116.05 | 122.04 |
| 88 | | 83.84 | 102.70 | 104.80 | 110.21 | 62 | 38 | 93.02 | 113.95 | 116.28 | 122.28 |
| 87 | | 84.02 | 102.92 | 105.03 | 110.45 | 63 | 37 | 93.20 | 114.17 | 116.51 | 122.52 |
| 86 | | 84.20 | 103.15 | 105.26 | 110.69 | 64 | 36 | 93.39 | 114.40 | 116.74 | 122.76 |
| 85 | | 84.39 | 103.38 | 105.49 | 110.93 | 65 | 35 | 93.57 | 114.62 | 116.96 | 123.00 |
| 84 | | 84.57 | 103.60 | 105.71 | 111.17 | 66 | 34 | 93.76 | 114.85 | 117.19 | 123.24 |
| 83 | | 84.75 | 103.82 | 105.94 | 111.41 | 67 | 33 | 93.94 | 115.08 | 117.42 | 123.49 |
| 82 | | 84.94 | 104.05 | 106.17 | 111.65 | 68 | 32 | 94.12 | 115.30 | 117.65 | 123.73 |
| 81 | | 85.12 | 104.27 | 106.40 | 111.90 | 69 | 31 | 94.31 | 115.53 | 117.88 | 123.97 |
| 80 | | 85.31 | 104.50 | 106.63 | 112.14 | 70 | 30 | 94.49 | 115.75 | 118.11 | 124.21 |
| 79 | | 85.49 | 104.73 | 106.86 | 112.38 | 71 | 29 | 94.67 | 115.97 | 118.34 | 124.45 |
| 78 | | 85.67 | 104.95 | 107.09 | 112.62 | 72 | 28 | 94.86 | 116.20 | 118.57 | 124.69 |
| 77 | | 85.86 | 105.18 | 107.32 | 112.86 | 73 | 27 | 95.04 | 116.42 | 118.80 | 124.93 |
| 76 | | 86.04 | 105.40 | 107.55 | 113.10 | 74 | 26 | 95.22 | 116.65 | 119.03 | 125.18 |
| 75 | | 86.22 | 105.62 | 107.78 | 113.34 | 75 | 25 | 95.41 | 116.88 | 119.26 | 125.42 |
| 74 | | 86.41 | 105.85 | 108.01 | 113.59 | 76 | 24 | 95.59 | 117.10 | 119.49 | 125.66 |
| 73 | | 86.59 | 106.07 | 108.24 | 113.83 | 77 | 23 | 95.78 | 117.33 | 119.72 | 125.90 |
| 72 | | 86.78 | 106.30 | 108.47 | 114.07 | 78 | 22 | 95.96 | 117.55 | 119.95 | 126.14 |
| 71 | | 86.96 | 106.53 | 108.70 | 114.31 | 79 | 21 | 96.14 | 117.77 | 120.18 | 126.38 |
| 70 | | 87.14 | 106.75 | 108.93 | 114.55 | 80 | 20 | 96.33 | 118.00 | 120.41 | 126.62 |
| 69 | | 87.33 | 106.98 | 109.16 | 114.79 | 81 | 19 | 96.51 | 118.22 | 120.64 | 126.86 |
| 68 | | 87.51 | 107.20 | 109.39 | 115.03 | 82 | 18 | 96.69 | 118.45 | 120.87 | 127.11 |
| 67 | | 87.69 | 107.42 | 109.62 | 115.28 | 83 | 17 | 96.88 | 118.68 | 121.10 | 127.35 |
| 66 | | 87.88 | 107.65 | 109.85 | 115.52 | 84 | 16 | 97.06 | 118.90 | 121.33 | 127.59 |
| 65 | | 88.06 | 107.87 | 110.08 | 115.76 | 85 | 15 | 97.25 | 119.13 | 121.56 | 127.83 |
| 64 | | 88.24 | 108.10 | 110.31 | 116.00 | 86 | 14 | 97.43 | 119.35 | 121.79 | 128.07 |
| 63 | | 88.43 | 108.32 | 110.54 | 116.24 | 87 | 13 | 97.61 | 119.57 | 122.02 | 128.31 |
| 62 | | 88.61 | 108.55 | 110.76 | 116.48 | 88 | 12 | 97.80 | 119.80 | 122.25 | 128.55 |
| 61 | | 88.80 | 108.77 | 110.99 | 116.73 | 89 | 11 | 97.98 | 120.03 | 122.48 | 128.80 |
| 60 | | 88.98 | 109.00 | 111.22 | 116.97 | 90 | 10 | 98.16 | 120.25 | 122.70 | 129.04 |
| 59 | | 89.16 | 109.22 | 111.45 | 117.21 | 91 | 9 | 98.35 | 120.48 | 122.93 | 129.28 |
| 58 | | 89.35 | 109.45 | 111.68 | 117.45 | 92 | 8 | 98.53 | 120.70 | 123.16 | 129.52 |
| 57 | | 89.53 | 109.67 | 111.91 | 117.69 | 93 | 7 | 98.71 | 120.92 | 123.39 | 129.76 |
| 56 | | 89.71 | 109.90 | 112.14 | 117.93 | 94 | 6 | 98.90 | 121.15 | 123.62 | 130.00 |
| 55 | | 89.90 | 110.13 | 112.37 | 118.17 | 95 | 5 | 99.08 | 121.37 | 123.85 | 130.25 |
| 54 | | 90.08 | 110.35 | 112.60 | 118.41 | 96 | 4 | 99.27 | 121.60 | 124.08 | 130.49 |
| 53 | | 90.27 | 110.58 | 112.83 | 118.66 | 97 | 3 | 99.45 | 121.83 | 124.31 | 130.73 |
| 52 | | 90.45 | 110.80 | 113.06 | 118.90 | 98 | 2 | 99.63 | 122.05 | 124.54 | 130.97 |
| 51 | | 90.63 | 111.02 | 113.29 | 119.14 | 99 | 1 | 99.82 | 122.28 | 124.77 | 131.21 |
| 50 | | | | | | 100 | 0 | 100.00 | 122.50 | 125.00 | 131.45 |

TABLE LXXXVI.—FUMING SULFURIC ACID

By C. WINKLER

| Specific Gravity 60°/60° F. | Total SO ₃ (Pts. per 100) | Free SO ₃ * | 100 Parts Contain H ₂ SO ₄ | 66° Bé. Acid |
|--------------------------------|---|------------------------|---|-----------------|
| 1.8337 | 75.31 | | 92.25 | 90.00 |
| 1.8387 | 77.38 | | 94.79 | 90.69 |
| 1.8437 | 79.28 | | 97.11 | 93.08 |
| 1.8487 | 80.01 | | 98.01 | 90.10 |
| 1.8537 | 80.95 | | 99.16 | 76.38 |
| 1.8587 | 81.84 | 1.54 | 98.40 | 72.81 |
| 1.8637 | 82.12 | 2.66 | 97.34 | 71.71 |
| 1.8687 | 82.41 | 4.28 | 95.76 | 70.53 |
| 1.8737 | 82.63 | 5.44 | 94.56 | 69.35 |
| 1.8787 | 82.81 | 6.42 | 93.58 | 68.92 |
| 1.8837 | 82.97 | 7.29 | 92.71 | 68.27 |
| 1.8887 | 83.13 | 8.16 | 91.94 | 67.55 |
| 1.8937 | 83.43 | 9.34 | 90.66 | 66.81 |
| 1.8987 | 83.48 | 10.07 | 89.93 | 66.24 |
| 1.9036 | 83.57 | 10.56 | 89.44 | 65.68 |
| 1.9086 | 83.73 | 11.43 | 88.57 | 65.25 |
| 1.9136 | 84.08 | 13.33 | 86.67 | 63.84 |
| 1.9186 | 84.56 | 15.95 | 84.05 | 62.10 |
| 1.9236 | 85.06 | 18.67 | 81.33 | 59.90 |
| 1.9286 | 85.57 | 21.34 | 78.66 | 57.80 |
| 1.9336 | 86.23 | 25.65 | 74.35 | 55.21 |
| 1.9386 | 86.78 | 28.03 | 71.97 | 53.00 |
| 1.9436 | 87.13 | 29.94 | 70.06 | 51.60 |
| 1.9486 | 87.41 | 31.46 | 68.54 | 50.48 |
| 1.9536 | 87.65 | 32.77 | 67.23 | 49.52 |
| 1.9586 | 88.22 | 35.87 | 64.13 | 47.23 |
| 1.9636 | 88.92 | 39.68 | 60.32 | 44.42 |
| 1.9686 | 89.83 | 44.61 | 55.36 | 40.78 |

* Amount of SO₃ which may be distilled off.

| Degrees Baumé | Specific Gravity 60°/60° F. | Per cent. H ₂ SO ₄ | Degrees Baumé | Specific Gravity 60°/60° F. | Per cent. H ₂ SO ₄ |
|------------------|--------------------------------|---|------------------|--------------------------------|---|
| 60 | 1.7059 | 77.67 | 64½ | 1.7957 | 86.33 |
| 61 | 1.7262 | 79.43 | 64½ | 1.8012 | 87.04 |
| 62 | 1.7470 | 81.30 | 64¾ | 1.8068 | 87.81 |
| 63 | 1.7683 | 83.34 | 65 | 1.8125 | 88.65 |
| 64 | 1.7901 | 85.66 | 65¼ | 1.8182 | 89.55 |
| | | | 65½ | 1.8239 | 90.60 |
| | | | 65¾ | 1.8297 | 91.80 |
| | | | 66 | 1.8354 | 93.19 |

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.
 From the Sp. Grs., the corresponding degrees Baumé were calculated by the following
 formula: Baumé = 145 — 145/Sp. Gr.

ALLOWANCE FOR TEMPERATURES

At 10° Bé. correction of 0.029° Bé. or 0.00023 Sp. Gr. for every 1° F.

| | | | | | | | | | |
|-----|---|---|---------|---|---------|---|---|---|-------|
| 20° | " | " | 0.036° | " | 0.00034 | " | " | " | 1° F. |
| 30° | " | " | 0.035° | " | 0.00039 | " | " | " | 1° F. |
| 40° | " | " | 0.031° | " | 0.00041 | " | " | " | 1° F. |
| 50° | " | " | 0.028° | " | 0.00045 | " | " | " | 1° F. |
| 60° | " | " | 0.026° | " | 0.00053 | " | " | " | 1° F. |
| 63° | " | " | 0.026° | " | 0.00057 | " | " | " | 1° F. |
| 66° | " | " | 0.0235° | " | 0.00054 | " | " | " | 1° F. |

For temperatures above 60° F., the correction is added to the observed indication;
 below 60° F., subtracted.

* Table 86 was approved and adopted as a standard by the Manufacturing Chem-
 ists' Association of the United States, June 23, 1904.

TABLE LXXXVII.—SULFURIC ACID

DENSITY (SPECIFIC GRAVITY) OF AQUEOUS SOLUTIONS AT $t^{\circ}/4^{\circ}$ C. FROM 0% TO 100% H_2SO_4 .
 THE DENSITY AT $t^{\circ}/15^{\circ}$ C. IS CALCULATED FOR WATER OF DENSITY 1.000868 AT 16° C.
 DOMKE: Abh. Norm.-Rich. Komm. 1904, 5, 5. Zts. anorg. Ch. 1905, 43, 125

| H_2SO_4 | 0° | 5° | 10° | 15° | 20° | 25° | 30° | 40° | 50° | n_D^{20} |
|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|------------|
| 0 | 0.9999 | 1.0000 | 0.9997 | 0.9991 | 0.9982 | 0.9971 | 0.9957 | 0.9922 | 0.9881 | 0.000 |
| 1 | 1.0075 | 1.0073 | 1.0069 | 1.0061 | 1.0051 | 1.0038 | 1.0022 | 0.9986 | 0.9944 | 0.205 |
| 2 | 1.0147 | 1.0144 | 1.0138 | 1.0129 | 1.0118 | 1.0104 | 1.0087 | 1.0050 | 1.0006 | 0.413 |
| 3 | 1.0219 | 1.0214 | 1.0206 | 1.0197 | 1.0184 | 1.0169 | 1.0152 | 1.0113 | 1.0067 | 0.624 |
| 4 | 1.0291 | 1.0284 | 1.0275 | 1.0264 | 1.0250 | 1.0234 | 1.0216 | 1.0176 | 1.0129 | 0.837 |
| 5 | 1.0364 | 1.0355 | 1.0344 | 1.0332 | 1.0317 | 1.0300 | 1.0281 | 1.0240 | 1.0192 | 1.053 |
| 6 | 1.0437 | 1.0426 | 1.0414 | 1.0400 | 1.0384 | 1.0367 | 1.0347 | 1.0305 | 1.0256 | 1.272 |
| 7 | 1.0511 | 1.0498 | 1.0485 | 1.0469 | 1.0453 | 1.0434 | 1.0414 | 1.0371 | 1.0321 | 1.494 |
| 8 | 1.0585 | 1.0571 | 1.0556 | 1.0539 | 1.0522 | 1.0502 | 1.0482 | 1.0437 | 1.0386 | 1.719 |
| 9 | 1.0660 | 1.0644 | 1.0628 | 1.0610 | 1.0591 | 1.0571 | 1.0549 | 1.0503 | 1.0451 | 1.947 |
| 10 | 1.0735 | 1.0718 | 1.0700 | 1.0681 | 1.0661 | 1.0640 | 1.0617 | 1.0570 | 1.0517 | 2.178 |
| 11 | 1.0810 | 1.0792 | 1.0773 | 1.0753 | 1.0731 | 1.0709 | 1.0686 | 1.0637 | 1.0584 | 2.412 |
| 12 | 1.0886 | 1.0866 | 1.0846 | 1.0825 | 1.0803 | 1.0780 | 1.0756 | 1.0705 | 1.0651 | 2.649 |
| 13 | 1.0962 | 1.0942 | 1.0920 | 1.0898 | 1.0874 | 1.0851 | 1.0826 | 1.0774 | 1.0719 | 2.889 |
| 14 | 1.1039 | 1.1017 | 1.0994 | 1.0971 | 1.0947 | 1.0922 | 1.0897 | 1.0844 | 1.0788 | 3.132 |
| 15 | 1.1116 | 1.1093 | 1.1069 | 1.1045 | 1.1020 | 1.0994 | 1.0968 | 1.0914 | 1.0857 | 3.378 |
| 16 | 1.1194 | 1.1170 | 1.1145 | 1.1120 | 1.1094 | 1.1067 | 1.1040 | 1.0985 | 1.0927 | 3.628 |
| 17 | 1.1272 | 1.1247 | 1.1221 | 1.1195 | 1.1168 | 1.1141 | 1.1113 | 1.1057 | 1.0998 | 3.881 |
| 18 | 1.1351 | 1.1325 | 1.1298 | 1.1270 | 1.1243 | 1.1215 | 1.1187 | 1.1129 | 1.1070 | 4.137 |
| 19 | 1.1430 | 1.1403 | 1.1375 | 1.1347 | 1.1318 | 1.1290 | 1.1261 | 1.1202 | 1.1142 | 4.396 |
| 20 | 1.1511 | 1.1481 | 1.1453 | 1.1424 | 1.1394 | 1.1365 | 1.1335 | 1.1275 | 1.1215 | 4.659 |
| 21 | 1.1590 | 1.1560 | 1.1531 | 1.1501 | 1.1471 | 1.1441 | 1.1411 | 1.1350 | 1.1288 | 4.925 |
| 22 | 1.1670 | 1.1640 | 1.1609 | 1.1579 | 1.1548 | 1.1517 | 1.1486 | 1.1424 | 1.1362 | 5.194 |
| 23 | 1.1751 | 1.1720 | 1.1688 | 1.1657 | 1.1626 | 1.1594 | 1.1563 | 1.1500 | 1.1437 | 5.467 |
| 24 | 1.1832 | 1.1800 | 1.1768 | 1.1736 | 1.1704 | 1.1672 | 1.1640 | 1.1576 | 1.1512 | 5.744 |
| 25 | 1.1914 | 1.1881 | 1.1848 | 1.1816 | 1.1783 | 1.1751 | 1.1718 | 1.1653 | 1.1588 | 6.024 |
| 26 | 1.1996 | 1.1962 | 1.1929 | 1.1896 | 1.1863 | 1.1829 | 1.1796 | 1.1730 | 1.1665 | 6.307 |
| 27 | 1.2078 | 1.2044 | 1.2010 | 1.1976 | 1.1942 | 1.1909 | 1.1875 | 1.1808 | 1.1742 | 6.594 |
| 28 | 1.2161 | 1.2126 | 1.2091 | 1.2057 | 1.2023 | 1.1989 | 1.1955 | 1.1887 | 1.1820 | 6.884 |
| 29 | 1.2243 | 1.2208 | 1.2173 | 1.2138 | 1.2104 | 1.2069 | 1.2035 | 1.1966 | 1.1898 | 7.178 |
| 30 | 1.2326 | 1.2291 | 1.2255 | 1.2220 | 1.2185 | 1.2150 | 1.2115 | 1.2046 | 1.1978 | 7.476 |
| 31 | 1.2410 | 1.2374 | 1.2338 | 1.2302 | 1.2267 | 1.2232 | 1.2196 | 1.2127 | 1.2057 | 7.777 |
| 32 | 1.2493 | 1.2457 | 1.2421 | 1.2385 | 1.2349 | 1.2314 | 1.2278 | 1.2207 | 1.2137 | 8.082 |
| 33 | 1.2577 | 1.2541 | 1.2504 | 1.2468 | 1.2432 | 1.2396 | 1.2360 | 1.2289 | 1.2219 | 8.390 |
| 34 | 1.2661 | 1.2625 | 1.2588 | 1.2552 | 1.2515 | 1.2479 | 1.2443 | 1.2371 | 1.2300 | 8.702 |
| 35 | 1.2746 | 1.2709 | 1.2672 | 1.2636 | 1.2599 | 1.2563 | 1.2527 | 1.2454 | 1.2383 | 9.018 |
| 36 | 1.2831 | 1.2794 | 1.2757 | 1.2720 | 1.2684 | 1.2647 | 1.2610 | 1.2538 | 1.2466 | 9.338 |
| 37 | 1.2917 | 1.2880 | 1.2843 | 1.2806 | 1.2769 | 1.2732 | 1.2695 | 1.2622 | 1.2549 | 9.662 |
| 38 | 1.3004 | 1.2966 | 1.2929 | 1.2891 | 1.2854 | 1.2817 | 1.2780 | 1.2707 | 1.2634 | 9.989 |
| 39 | 1.3091 | 1.3053 | 1.3016 | 1.2978 | 1.2941 | 1.2904 | 1.2866 | 1.2793 | 1.2719 | 10.322 |
| 40 | 1.3179 | 1.3141 | 1.3103 | 1.3065 | 1.3028 | 1.2991 | 1.2953 | 1.2879 | 1.2806 | 10.657 |
| 41 | 1.3267 | 1.3229 | 1.3191 | 1.3153 | 1.3116 | 1.3078 | 1.3041 | 1.2967 | 1.2893 | 10.997 |
| 42 | 1.3357 | 1.3318 | 1.3280 | 1.3242 | 1.3204 | 1.3167 | 1.3129 | 1.3055 | 1.2981 | 11.341 |
| 43 | 1.3447 | 1.3408 | 1.3370 | 1.3332 | 1.3294 | 1.3256 | 1.3218 | 1.3144 | 1.3070 | 11.690 |
| 44 | 1.3538 | 1.3500 | 1.3461 | 1.3423 | 1.3384 | 1.3346 | 1.3309 | 1.3234 | 1.3160 | 12.043 |
| 45 | 1.3631 | 1.3592 | 1.3553 | 1.3514 | 1.3476 | 1.3438 | 1.3400 | 1.3325 | 1.3250 | 12.401 |
| 46 | 1.3724 | 1.3685 | 1.3646 | 1.3607 | 1.3569 | 1.3530 | 1.3492 | 1.3417 | 1.3342 | 12.764 |
| 47 | 1.3819 | 1.3779 | 1.3740 | 1.3701 | 1.3663 | 1.3624 | 1.3586 | 1.3510 | 1.3435 | 13.131 |
| 48 | 1.3915 | 1.3875 | 1.3836 | 1.3796 | 1.3757 | 1.3719 | 1.3680 | 1.3604 | 1.3528 | 13.504 |
| 49 | 1.4012 | 1.3972 | 1.3932 | 1.3893 | 1.3853 | 1.3814 | 1.3776 | 1.3699 | 1.3623 | 13.881 |
| 50 | 1.4110 | 1.4070 | 1.4030 | 1.3990 | 1.3951 | 1.3911 | 1.3872 | 1.3795 | 1.3719 | 14.264 |
| 51 | 1.4209 | 1.4169 | 1.4128 | 1.4088 | 1.4049 | 1.4009 | 1.3970 | 1.3893 | 1.3816 | 14.652 |
| 52 | 1.4310 | 1.4269 | 1.4228 | 1.4188 | 1.4148 | 1.4109 | 1.4069 | 1.3991 | 1.3914 | 15.045 |
| 53 | 1.4411 | 1.4370 | 1.4330 | 1.4289 | 1.4249 | 1.4209 | 1.4169 | 1.4091 | 1.4013 | 15.443 |
| 54 | 1.4514 | 1.4473 | 1.4432 | 1.4391 | 1.4350 | 1.4310 | 1.4270 | 1.4191 | 1.4113 | 15.846 |
| 55 | 1.4618 | 1.4577 | 1.4536 | 1.4494 | 1.4453 | 1.4412 | 1.4372 | 1.4293 | 1.4214 | 16.255 |

n_D^{20} = molecular equivalent or normality of sulfuric acid solution at 15° C. (1 equivalent = 49.0 grams of H_2SO_4 per liter), corresponding to the percentage figures in the column on the extreme left, which is the g. of H_2SO_4 in 100 g. of solution.

TABLE LXXXVII. (Concluded)

| $\frac{\%}{\text{H}_2\text{SO}_4}$ | 0° | 5° | 10° | 15° | 20° | 25° | 30° | 40° | 50° | n^1 |
|------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 56 | 1.4724 | 1.4681 | 1.4640 | 1.4598 | 1.4557 | 1.4516 | 1.4475 | 1.4395 | 1.4317 | 18.670 |
| 57 | 1.4830 | 1.4787 | 1.4745 | 1.4703 | 1.4662 | 1.4620 | 1.4580 | 1.4499 | 1.4420 | 17.090 |
| 58 | 1.4937 | 1.4894 | 1.4851 | 1.4809 | 1.4767 | 1.4726 | 1.4685 | 1.4604 | 1.4524 | 17.515 |
| 59 | 1.5045 | 1.5002 | 1.4959 | 1.4916 | 1.4874 | 1.4832 | 1.4791 | 1.4709 | 1.4629 | 17.946 |
| 60 | 1.5154 | 1.5111 | 1.5067 | 1.5024 | 1.4982 | 1.4940 | 1.4898 | 1.4816 | 1.4735 | 18.382 |
| 61 | 1.5264 | 1.5220 | 1.5177 | 1.5133 | 1.5091 | 1.5048 | 1.5006 | 1.4923 | 1.4842 | 18.824 |
| 62 | 1.5376 | 1.5331 | 1.5287 | 1.5243 | 1.5200 | 1.5157 | 1.5115 | 1.5031 | 1.4949 | 19.272 |
| 63 | 1.5487 | 1.5442 | 1.5398 | 1.5354 | 1.5310 | 1.5267 | 1.5224 | 1.5140 | 1.5058 | 19.725 |
| 64 | 1.5600 | 1.5555 | 1.5510 | 1.5465 | 1.5421 | 1.5378 | 1.5335 | 1.5250 | 1.5167 | 20.183 |
| 65 | 1.5713 | 1.5668 | 1.5622 | 1.5578 | 1.5533 | 1.5490 | 1.5446 | 1.5361 | 1.5277 | 20.647 |
| 66 | 1.5828 | 1.5782 | 1.5736 | 1.5691 | 1.5646 | 1.5602 | 1.5558 | 1.5472 | 1.5388 | 21.117 |
| 67 | 1.5943 | 1.5896 | 1.5850 | 1.5805 | 1.5760 | 1.5715 | 1.5671 | 1.5584 | 1.5499 | 21.593 |
| 68 | 1.6058 | 1.6012 | 1.5965 | 1.5919 | 1.5874 | 1.5829 | 1.5784 | 1.5697 | 1.5611 | 22.075 |
| 69 | 1.6175 | 1.6128 | 1.6081 | 1.6035 | 1.5989 | 1.5944 | 1.5899 | 1.5811 | 1.5725 | 22.562 |
| 70 | 1.6293 | 1.6245 | 1.6198 | 1.6151 | 1.6105 | 1.6059 | 1.6014 | 1.5925 | 1.5838 | 23.054 |
| 71 | 1.6411 | 1.6363 | 1.6315 | 1.6268 | 1.6221 | 1.6175 | 1.6130 | 1.6040 | 1.5952 | 23.553 |
| 72 | 1.6529 | 1.6481 | 1.6433 | 1.6385 | 1.6339 | 1.6292 | 1.6246 | 1.6156 | 1.6067 | 24.057 |
| 73 | 1.6649 | 1.6600 | 1.6551 | 1.6503 | 1.6456 | 1.6409 | 1.6363 | 1.6271 | 1.6182 | 24.567 |
| 74 | 1.6768 | 1.6719 | 1.6670 | 1.6622 | 1.6574 | 1.6526 | 1.6480 | 1.6387 | 1.6297 | 25.082 |
| 75 | 1.6888 | 1.6838 | 1.6789 | 1.6740 | 1.6692 | 1.6644 | 1.6597 | 1.6503 | 1.6412 | 25.602 |
| 76 | 1.7008 | 1.6958 | 1.6908 | 1.6858 | 1.6810 | 1.6761 | 1.6713 | 1.6610 | 1.6526 | 26.126 |
| 77 | 1.7127 | 1.7077 | 1.7026 | 1.6976 | 1.6927 | 1.6878 | 1.6829 | 1.6734 | 1.6640 | 26.655 |
| 78 | 1.7247 | 1.7195 | 1.7144 | 1.7093 | 1.7043 | 1.6994 | 1.6944 | 1.6847 | 1.6751 | 27.188 |
| 79 | 1.7366 | 1.7313 | 1.7261 | 1.7209 | 1.7159 | 1.7108 | 1.7058 | 1.6959 | 1.6862 | 27.724 |
| 80 | 1.7482 | 1.7429 | 1.7376 | 1.7324 | 1.7272 | 1.7221 | 1.7170 | 1.7069 | 1.6971 | 28.261 |
| 81 | 1.7597 | 1.7542 | 1.7489 | 1.7435 | 1.7383 | 1.7331 | 1.7279 | 1.7177 | 1.7077 | 28.799 |
| 82 | 1.7709 | 1.7654 | 1.7599 | 1.7544 | 1.7491 | 1.7437 | 1.7385 | 1.7281 | 1.7180 | 29.336 |
| 83 | 1.7816 | 1.7759 | 1.7704 | 1.7649 | 1.7594 | 1.7540 | 1.7487 | 1.7382 | 1.7279 | 29.871 |
| 84 | 1.7916 | 1.7860 | 1.7804 | 1.7748 | 1.7693 | 1.7639 | 1.7585 | 1.7479 | 1.7375 | 30.401 |
| 85 | 1.8009 | 1.7953 | 1.7897 | 1.7841 | 1.7786 | 1.7732 | 1.7678 | 1.7571 | 1.7466 | 30.924 |
| 86 | 1.8095 | 1.8039 | 1.7983 | 1.7927 | 1.7872 | 1.7818 | 1.7763 | 1.7657 | 1.7552 | 31.438 |
| 87 | 1.8173 | 1.8117 | 1.8061 | 1.8006 | 1.7951 | 1.7897 | 1.7843 | 1.7736 | 1.7632 | 31.943 |
| 88 | 1.8243 | 1.8187 | 1.8132 | 1.8077 | 1.8022 | 1.7968 | 1.7915 | 1.7809 | 1.7705 | 32.438 |
| 89 | 1.8306 | 1.8250 | 1.8195 | 1.8141 | 1.8087 | 1.8033 | 1.7979 | 1.7874 | 1.7770 | 32.929 |
| 90 | 1.8361 | 1.8306 | 1.8252 | 1.8198 | 1.8144 | 1.8091 | 1.8038 | 1.7933 | 1.7829 | 33.397 |
| 91 | 1.8410 | 1.8356 | 1.8302 | 1.8248 | 1.8195 | 1.8142 | 1.8090 | 1.7986 | 1.7883 | 33.862 |
| 92 | 1.8453 | 1.8399 | 1.8346 | 1.8293 | 1.8240 | 1.8188 | 1.8136 | 1.8033 | 1.7932 | 34.318 |
| 93 | 1.8490 | 1.8437 | 1.8384 | 1.8331 | 1.8279 | 1.8227 | 1.8176 | 1.8074 | 1.7974 | 34.764 |
| 94 | 1.8520 | 1.8467 | 1.8415 | 1.8363 | 1.8312 | 1.8260 | 1.8210 | 1.8110 | 1.8011 | 35.199 |
| 95 | 1.8544 | 1.8491 | 1.8439 | 1.8388 | 1.8337 | 1.8286 | 1.8236 | 1.8137 | 1.8040 | 35.622 |
| 96 | 1.8560 | 1.8508 | 1.8457 | 1.8406 | 1.8355 | 1.8305 | 1.8255 | 1.8157 | 1.8060 | 36.030 |
| 97 | 1.8569 | 1.8517 | 1.8466 | 1.8414 | 1.8364 | 1.8314 | 1.8264 | 1.8166 | 1.8071 | 36.421 |
| 98 | 1.8567 | 1.8515 | 1.8463 | 1.8411 | 1.8361 | 1.8310 | 1.8261 | 1.8163 | 1.8068 | 36.791 |
| 99 | 1.8551 | 1.8498 | 1.8445 | 1.8393 | 1.8342 | 1.8292 | 1.8242 | 1.8145 | 1.8050 | 37.133 |
| 100 | (1.8517) | (1.8463) | (1.8409) | (1.8357) | (1.8305) | (1.8255) | (1.8205) | (1.8107) | (1.8013) | (37.433) |

n^1 = molecular equivalent or normality of sulfuric acid solution at 15° C. (1 equivalent = 49.04 grams of H_2SO_4 per liter), corresponding to the percentage figures in the column on the extreme left, which is the grams of H_2SO_4 in 100 grams of solution.

TABLE LXXXVIII.—SULFURIC ACID

| Degrees Densities Baumé Twaddell | Specific Gravity 60°/60° | Lb. Av. Cu. Ft. | % SO ₃ | Lb. SO ₃ Cu. Ft. | % H ₂ SO ₄ | Lb. H ₂ SO ₄ Cu. Ft. | % Free H ₂ O | % Com- bined H ₂ O | % O. V. | Lb. O. V. in 1 Cu. Ft. | Freezing (Melting) Points ° F. | ° C. |
|-------------------------------------|-----------------------------|--------------------|----------------------|--------------------------------|-------------------------------------|---|-------------------------------|--|------------|------------------------------|--------------------------------------|-------|
| | | | | | | | | | | | | |
| 1 | 1.38 | 1.0069 | 0.83 | 0.52 | 1.02 | 0.64 | 98.98 | 0.19 | 1.09 | 0.68 | 31.2 | -0.4 |
| 2 | 2.80 | 1.0140 | 1.70 | 1.08 | 2.08 | 1.32 | 97.92 | 0.38 | 2.23 | 1.41 | 30.5 | -0.8 |
| 3 | 4.22 | 1.0211 | 2.56 | 1.63 | 3.13 | 1.99 | 96.87 | 0.57 | 3.38 | 2.14 | 29.8 | -1.2 |
| 4 | 5.64 | 1.0282 | 3.41 | 2.18 | 4.18 | 2.70 | 95.79 | 0.77 | 4.52 | 2.90 | 28.9 | -1.7 |
| 5 | 7.06 | 1.0353 | 4.26 | 2.73 | 5.23 | 3.41 | 94.62 | 0.97 | 5.67 | 3.66 | 28.1 | -2.2 |
| 6 | 8.48 | 1.0424 | 5.11 | 3.28 | 6.30 | 4.11 | 93.46 | 1.17 | 6.82 | 4.44 | 27.2 | -2.7 |
| 7 | 9.90 | 1.0495 | 5.96 | 3.83 | 7.37 | 4.85 | 92.25 | 1.37 | 7.99 | 5.24 | 26.3 | -3.2 |
| 8 | 11.32 | 1.0566 | 6.81 | 4.38 | 8.44 | 5.59 | 91.00 | 1.57 | 9.17 | 6.06 | 25.4 | -3.8 |
| 9 | 12.74 | 1.0637 | 7.66 | 4.93 | 9.51 | 6.33 | 89.75 | 1.77 | 10.37 | 6.89 | 24.5 | -4.4 |
| 10 | 14.16 | 1.0708 | 8.51 | 5.48 | 10.58 | 7.07 | 88.50 | 1.98 | 11.56 | 7.74 | 23.6 | -5.0 |
| 11 | 15.58 | 1.0779 | 9.36 | 6.03 | 11.75 | 7.81 | 87.25 | 2.18 | 12.76 | 8.61 | 22.7 | -5.6 |
| 12 | 17.00 | 1.0850 | 10.21 | 6.58 | 12.92 | 8.55 | 86.00 | 2.39 | 13.96 | 9.49 | 21.8 | -6.2 |
| 13 | 18.42 | 1.0921 | 11.06 | 7.13 | 14.09 | 9.29 | 84.75 | 2.59 | 15.16 | 10.39 | 20.9 | -6.7 |
| 14 | 19.84 | 1.0992 | 11.91 | 7.68 | 15.26 | 10.03 | 83.50 | 2.80 | 16.36 | 11.28 | 19.9 | -7.3 |
| 15 | 21.26 | 1.1063 | 12.76 | 8.23 | 16.43 | 10.77 | 82.25 | 3.01 | 17.56 | 12.18 | 19.0 | -7.9 |
| 16 | 22.68 | 1.1134 | 13.61 | 8.78 | 17.60 | 11.51 | 81.00 | 3.22 | 18.76 | 13.08 | 18.1 | -8.5 |
| 17 | 24.10 | 1.1205 | 14.46 | 9.33 | 18.77 | 12.25 | 79.75 | 3.43 | 19.96 | 13.98 | 17.2 | -9.1 |
| 18 | 25.52 | 1.1276 | 15.31 | 9.88 | 19.94 | 13.00 | 78.50 | 3.64 | 21.16 | 14.88 | 16.3 | -9.7 |
| 19 | 26.94 | 1.1347 | 16.16 | 10.43 | 21.11 | 13.74 | 77.25 | 3.85 | 22.36 | 15.78 | 15.4 | -10.3 |
| 20 | 28.36 | 1.1418 | 17.01 | 10.98 | 22.28 | 14.48 | 76.00 | 4.06 | 23.56 | 16.68 | 14.5 | -10.9 |
| 21 | 29.78 | 1.1489 | 17.86 | 11.53 | 23.45 | 15.22 | 74.75 | 4.27 | 24.76 | 17.58 | 13.6 | -11.5 |
| 22 | 31.20 | 1.1560 | 18.71 | 12.08 | 24.62 | 15.96 | 73.50 | 4.48 | 25.96 | 18.48 | 12.7 | -12.1 |
| 23 | 32.62 | 1.1631 | 19.56 | 12.63 | 25.79 | 16.70 | 72.25 | 4.69 | 27.16 | 19.38 | 11.8 | -12.7 |
| 24 | 34.04 | 1.1702 | 20.41 | 13.18 | 26.96 | 17.44 | 71.00 | 4.90 | 28.36 | 20.28 | 10.9 | -13.3 |
| 25 | 35.46 | 1.1773 | 21.26 | 13.73 | 28.13 | 18.18 | 69.75 | 5.11 | 29.56 | 21.18 | 10.0 | -13.9 |
| 26 | 36.88 | 1.1844 | 22.11 | 14.28 | 29.30 | 18.92 | 68.50 | 5.32 | 30.76 | 22.08 | 9.1 | -14.5 |
| 27 | 38.30 | 1.1915 | 22.96 | 14.83 | 30.47 | 19.66 | 67.25 | 5.53 | 31.96 | 22.98 | 8.2 | -15.1 |
| 28 | 39.72 | 1.1986 | 23.81 | 15.38 | 31.64 | 20.40 | 66.00 | 5.74 | 33.16 | 23.88 | 7.3 | -15.7 |
| 29 | 41.14 | 1.2057 | 24.66 | 15.93 | 32.81 | 21.14 | 64.75 | 5.95 | 34.36 | 24.78 | 6.4 | -16.3 |
| 30 | 42.56 | 1.2128 | 25.51 | 16.48 | 33.98 | 21.88 | 63.50 | 6.16 | 35.56 | 25.68 | 5.5 | -16.9 |
| 31 | 43.98 | 1.2199 | 26.36 | 17.03 | 35.15 | 22.62 | 62.25 | 6.37 | 36.76 | 26.58 | 4.6 | -17.5 |
| 32 | 45.40 | 1.2270 | 27.21 | 17.58 | 36.32 | 23.36 | 61.00 | 6.58 | 37.96 | 27.48 | 3.7 | -18.1 |
| 33 | 46.82 | 1.2341 | 28.06 | 18.13 | 37.49 | 24.10 | 59.75 | 6.79 | 39.16 | 28.38 | 2.8 | -18.7 |
| 34 | 48.24 | 1.2412 | 28.91 | 18.68 | 38.66 | 24.84 | 58.50 | 7.00 | 40.36 | 29.28 | 1.9 | -19.3 |
| 35 | 49.66 | 1.2483 | 29.76 | 19.23 | 39.83 | 25.58 | 57.25 | 7.21 | 41.56 | 30.18 | 1.0 | -19.9 |
| 36 | 51.08 | 1.2554 | 30.61 | 19.78 | 40.99 | 26.32 | 56.00 | 7.42 | 42.76 | 31.08 | 0.1 | -20.5 |
| 37 | 52.50 | 1.2625 | 31.46 | 20.33 | 42.16 | 27.06 | 54.75 | 7.63 | 43.96 | 31.98 | -0.8 | -21.1 |
| 38 | 53.92 | 1.2696 | 32.31 | 20.88 | 43.33 | 27.80 | 53.50 | 7.84 | 45.16 | 32.88 | -1.7 | -21.7 |
| 39 | 55.34 | 1.2767 | 33.16 | 21.43 | 44.50 | 28.54 | 52.25 | 8.05 | 46.36 | 33.78 | -2.6 | -22.3 |
| 40 | 56.76 | 1.2838 | 34.01 | 21.98 | 45.67 | 29.28 | 51.00 | 8.26 | 47.56 | 34.68 | -3.5 | -22.9 |

TABLE LXXXVIII.—SULFURIC ACID—(Continued)

| ° B. | Degrees Twaddell | Specific Gravity 60°/60° F. | Lb. Av. per Cu. Ft. | SO ₃ C. | Lb. SO ₃ per Cu. Ft. | H ₂ SO ₄ C. | Lb. H ₂ SO ₄ per Cu. Ft. | H ₂ SO ₄ C. | Percent Free H ₂ O | Percent Com- bined H ₂ O | O. V. C. | Lb. O. V. per Cu. Ft. | Freezing (Melt- ing) Points ° F. ° C. |
|------|---------------------|--------------------------------------|---------------------------|-----------------------|---------------------------------------|--------------------------------------|--|--------------------------------------|-------------------------------------|--|-------------|-----------------------------|---|
| 40 | 76.20 | 1.3810 | 86.13 | 39.27 | 33.82 | 48.10 | 41.43 | | 51.90 | 8.83 | 51.61 | 44.45 | -40.6 |
| 41 | 75.84 | 1.3842 | 86.96 | 40.38 | 33.51 | 49.47 | 43.02 | | 50.53 | 9.09 | 53.08 | 46.16 | -37.2 |
| 42 | 81.32 | 1.4078 | 87.80 | 41.53 | 36.46 | 50.87 | 44.66 | | 49.13 | 9.36 | 54.88 | 47.82 | -33.0 |
| 43 | 84.32 | 1.4216 | 88.67 | 42.66 | 37.83 | 52.26 | 46.04 | | 47.74 | 9.64 | 56.67 | 49.52 | -29.0 |
| 44 | 87.12 | 1.4356 | 89.54 | 43.80 | 39.23 | 53.65 | 47.43 | | 46.34 | 9.89 | 57.58 | 51.36 | -23.0 |
| 45 | 89.92 | 1.4496 | 90.41 | 44.96 | 40.65 | 55.07 | 49.81 | | 44.93 | 10.11 | 59.09 | 53.44 | -20.0 |
| 46 | 92.92 | 1.4636 | 91.35 | 46.11 | 42.12 | 56.48 | 51.39 | | 43.52 | 10.37 | 60.60 | 55.39 | -14.0 |
| 47 | 95.92 | 1.4776 | 92.28 | 47.27 | 43.62 | 57.90 | 53.43 | | 42.10 | 10.63 | 62.13 | 57.33 | -10.0 |
| 48 | 98.96 | 1.4918 | 93.23 | 48.43 | 45.10 | 59.32 | 55.30 | | 40.68 | 10.89 | 63.65 | 59.34 | -6.0 |
| 49 | 102.03 | 1.5101 | 94.20 | 49.59 | 46.71 | 60.75 | 57.23 | | 39.25 | 11.15 | 65.18 | 61.30 | -2.0 |
| 50 | 105.26 | 1.5263 | 95.20 | 50.76 | 48.32 | 62.16 | 59.16 | | 37.83 | 11.40 | 66.72 | 63.32 | 32.8 |
| 51 | 108.52 | 1.5426 | 96.21 | 51.91 | 49.93 | 63.56 | 61.09 | | 36.41 | 11.69 | 68.31 | 65.72 | 36.1 |
| 52 | 111.82 | 1.5591 | 97.24 | 53.17 | 51.70 | 65.03 | 63.33 | | 34.97 | 11.96 | 69.89 | 67.96 | 39.4 |
| 53 | 115.22 | 1.5758 | 98.30 | 54.50 | 53.47 | 66.63 | 65.49 | | 33.57 | 12.24 | 71.50 | 70.25 | 45.0 |
| 54 | 118.68 | 1.5934 | 99.38 | 55.62 | 55.28 | 68.13 | 67.71 | | 31.87 | 12.51 | 73.11 | 72.66 | 50.6 |
| 55 | 122.22 | 1.6111 | 100.48 | 56.86 | 57.13 | 69.65 | 69.98 | | 30.35 | 12.79 | 74.73 | 75.00 | Below |
| 56 | 125.84 | 1.6292 | 101.61 | 58.10 | 59.04 | 71.17 | 72.22 | | 29.23 | 13.06 | 76.37 | 77.40 | -40 |
| 57 | 129.54 | 1.6477 | 102.77 | 59.39 | 61.04 | 72.72 | 74.73 | | 28.23 | 13.36 | 78.07 | 80.23 | |
| 58 | 133.33 | 1.6667 | 103.93 | 60.70 | 63.10 | 74.36 | 77.30 | | 27.23 | 13.66 | 79.79 | 82.65 | |
| 59 | 137.18 | 1.6860 | 105.16 | 62.03 | 65.23 | 75.99 | 79.91 | | 26.01 | 13.96 | 81.54 | 85.75 | |
| 60 | 141.18 | 1.7059 | 106.40 | 63.40 | 67.46 | 77.67 | 82.64 | | 24.61 | 14.27 | 83.35 | 88.98 | |
| 61 | 145.24 | 1.7262 | 107.66 | 64.84 | 69.81 | 79.43 | 85.51 | | 23.33 | 14.59 | 85.23 | 91.76 | |
| 62 | 149.40 | 1.7470 | 108.96 | 66.37 | 72.31 | 81.30 | 88.58 | | 22.37 | 14.89 | 87.14 | 94.63 | |
| 63 | 153.66 | 1.7683 | 110.29 | 68.03 | 75.03 | 83.14 | 91.52 | | 18.70 | 15.33 | 89.44 | 98.63 | |
| 64 | 158.02 | 1.7901 | 111.65 | 69.87 | 77.83 | 85.04 | 94.69 | | 14.31 | 15.74 | 91.92 | 102.63 | |
| 65 | 162.44 | 1.8124 | 113.05 | 70.97 | 79.93 | 86.93 | 96.99 | | 13.67 | 15.86 | 92.64 | 103.75 | |
| 66 | 166.24 | 1.8312 | 113.34 | 71.05 | 79.82 | 87.04 | 97.78 | | 12.96 | 15.99 | 93.40 | 104.93 | |
| 67 | 169.36 | 1.8498 | 113.69 | 71.68 | 80.78 | 87.81 | 98.95 | | 12.19 | 16.13 | 94.23 | 106.19 | |
| 68 | 172.60 | 1.8683 | 114.05 | 72.37 | 81.81 | 88.65 | 100.22 | | 11.35 | 16.28 | 95.13 | 107.67 | |
| 69 | 175.94 | 1.8852 | 114.40 | 73.10 | 82.90 | 89.55 | 101.55 | | 10.45 | 16.45 | 96.07 | 109.22 | |
| 70 | 179.34 | 1.9024 | 114.76 | 73.96 | 84.14 | 90.50 | 103.07 | | 8.20 | 16.86 | 98.51 | 112.42 | |
| 71 | 182.84 | 1.9197 | 115.12 | 74.87 | 85.42 | 91.50 | 104.67 | | 6.00 | 17.12 | 100.87 | 115.64 | |
| 72 | 186.48 | 1.9374 | 115.48 | 75.82 | 86.78 | 92.50 | 106.37 | | 5.00 | 17.46 | 103.01 | 117.63 | |
| 73 | 190.24 | 1.9554 | 115.84 | 76.82 | 88.03 | 93.50 | 108.06 | | 4.00 | 17.62 | 103.01 | 118.49 | |
| 74 | 194.12 | 1.9737 | 116.20 | 77.87 | 89.03 | 94.50 | 109.76 | | 3.00 | 17.92 | 104.63 | 120.32 | |
| 75 | 198.12 | 1.9924 | 116.56 | 78.97 | 90.07 | 95.00 | 110.33 | | 2.00 | 18.00 | 105.16 | 122.07 | |
| 76 | 202.24 | 2.0114 | 116.93 | 79.37 | 90.07 | 96.00 | 111.54 | | 1.00 | 18.18 | 106.23 | 123.06 | |
| 77 | 206.48 | 2.0307 | 117.30 | 80.07 | 91.05 | 97.00 | 112.63 | | 0.00 | 18.37 | 107.31 | | |
| 78 | 210.84 | 2.0503 | 117.67 | 80.87 | 91.53 | 97.00 | 113.54 | | | | | | |
| 79 | 215.32 | 2.0703 | 118.04 | 81.67 | 92.00 | 98.00 | 114.40 | | | | | | |
| 80 | 219.92 | 2.0906 | 118.41 | 82.47 | 92.47 | 99.00 | 115.26 | | | | | | |
| 81 | 224.64 | 2.1112 | 118.78 | 83.27 | 93.00 | 100.00 | 116.10 | | | | | | |
| 82 | 229.48 | 2.1322 | 119.15 | 84.07 | 93.53 | 100.00 | 116.93 | | | | | | |
| 83 | 234.44 | 2.1534 | 119.52 | 84.87 | 94.06 | 100.00 | 117.76 | | | | | | |
| 84 | 239.52 | 2.1750 | 120.00 | 85.67 | 94.59 | 100.00 | 118.58 | | | | | | |
| 85 | 244.72 | 2.1968 | 120.37 | 86.47 | 95.12 | 100.00 | 119.40 | | | | | | |
| 86 | 249.96 | 2.2189 | 120.74 | 87.27 | 95.65 | 100.00 | 120.22 | | | | | | |
| 87 | 255.32 | 2.2413 | 121.11 | 88.07 | 96.18 | 100.00 | 121.04 | | | | | | |
| 88 | 260.80 | 2.2640 | 121.48 | 88.87 | 96.71 | 100.00 | 121.86 | | | | | | |
| 89 | 266.40 | 2.2870 | 121.85 | 89.67 | 97.24 | 100.00 | 122.68 | | | | | | |
| 90 | 272.12 | 2.3103 | 122.22 | 90.47 | 97.77 | 100.00 | 123.50 | | | | | | |
| 91 | 277.96 | 2.3339 | 122.59 | 91.27 | 98.30 | 100.00 | 124.32 | | | | | | |
| 92 | 283.92 | 2.3578 | 122.96 | 92.07 | 98.83 | 100.00 | 125.14 | | | | | | |
| 93 | 289.96 | 2.3819 | 123.33 | 92.87 | 99.36 | 100.00 | 125.96 | | | | | | |
| 94 | 296.12 | 2.4063 | 123.70 | 93.67 | 99.89 | 100.00 | 126.78 | | | | | | |
| 95 | 302.40 | 2.4310 | 124.07 | 94.47 | 100.42 | 100.00 | 127.60 | | | | | | |
| 96 | 308.80 | 2.4560 | 124.44 | 95.27 | 100.95 | 100.00 | 128.42 | | | | | | |
| 97 | 315.32 | 2.4812 | 124.81 | 96.07 | 101.48 | 100.00 | 129.24 | | | | | | |
| 98 | 321.96 | 2.5067 | 125.18 | 96.87 | 102.01 | 100.00 | 130.06 | | | | | | |
| 99 | 328.72 | 2.5324 | 125.55 | 97.67 | 102.54 | 100.00 | 130.88 | | | | | | |
| 100 | 335.60 | 2.5583 | 125.92 | 98.47 | 103.07 | 100.00 | 131.70 | | | | | | |

TABLE LXXXVIII.—SULFURIC ACID (Concluded)

| Degrees Baumé | Per cent. H ₂ SO ₄ | 0° Bé. 100% H ₂ SO ₄ Per cent. 60° Bé | Lb. 60° in 1 Cu. Ft. | Per cent. 50° Bé | Lb. 50° in 1 Cu. Ft. |
|------------------|---|---|-------------------------|---------------------|-------------------------|
| 40 | | 61.93 | 53.34 | 77.36 | 66.63 |
| 41 | | 63.69 | 55.39 | 79.59 | 69.19 |
| 42 | | 65.50 | 57.50 | 81.81 | 71.83 |
| 43 | | 67.28 | 59.66 | 84.05 | 74.53 |
| 44 | | 69.09 | 61.86 | 86.30 | 77.27 |
| 45 | | 70.90 | 64.12 | 88.56 | 80.10 |
| 46 | | 72.72 | 66.43 | 90.83 | 82.98 |
| 47 | | 74.55 | 68.79 | 93.12 | 85.93 |
| 48 | | 76.37 | 71.20 | 95.40 | 88.94 |
| 49 | | 78.22 | 73.68 | 97.70 | 92.03 |
| 50 | | 80.06 | 76.21 | 100.00 | 95.20 |
| 51 | | 81.96 | 78.85 | 102.38 | 98.50 |
| 52 | | 83.86 | 81.54 | 104.74 | 101.85 |
| 53 | | 85.79 | 84.33 | 107.15 | 105.33 |
| 54 | | 87.72 | 87.17 | 109.57 | 108.89 |
| 55 | | 89.67 | 90.10 | 112.01 | 112.55 |
| 56 | | 91.63 | 93.11 | 114.46 | 116.30 |
| 57 | | 93.67 | 96.26 | 117.00 | 120.24 |
| 58 | | 95.74 | 99.52 | 119.59 | 124.31 |
| 59 | | 97.84 | 102.89 | 122.21 | 128.52 |
| 60 | | 100.00 | 106.40 | 124.91 | 132.91 |
| 61 | | 102.27 | 110.10 | 127.74 | 137.52 |
| 62 | | 104.67 | 114.05 | 130.75 | 142.47 |
| 63 | | 107.30 | 118.34 | 134.03 | 147.82 |
| 64 | | 110.29 | 123.44 | 137.76 | 153.81 |
| 64½ | | 111.15 | 124.49 | 138.84 | 155.50 |
| 64½ | | 112.06 | 125.89 | 139.98 | 157.25 |
| 64½ | | 113.05 | 127.40 | 141.22 | 159.14 |
| 65 | | 114.14 | 129.03 | 142.57 | 161.17 |
| 65½ | | 115.30 | 130.75 | 144.02 | 163.32 |
| 65½ | | 116.65 | 132.70 | 145.71 | 165.76 |
| 65½ | | 118.19 | 134.88 | 147.63 | 168.48 |
| 66 | | 119.98 | 137.34 | 149.87 | 171.56 |
| .. | 94.00 | 121.02 | 138.74 | 151.17 | 173.30 |
| .. | 95.00 | 122.31 | 140.41 | 152.78 | 175.39 |
| .. | 96.00 | 123.60 | 142.05 | 154.39 | 177.44 |
| .. | 97.00 | 124.89 | 143.61 | 156.00 | 179.38 |
| .. | 98.00 | 126.17 | 145.08 | 157.61 | 181.24 |
| .. | 99.00 | 126.46 | 145.32 | 159.22 | 182.96 |
| .. | 100.00 | 128.75 | 147.68 | 160.82 | 184.46 |

ALLOWANCE FOR TEMPERATURE

| Strength | Per Degree Fahrenheit | Per Degree Centigrade |
|-------------------------------------|-----------------------------|----------------------------|
| 10° Bé. | 0.029° Bé. 0.00023 sp. gr. | 0.052° Bé. 0.00041 sp. gr. |
| 20° Bé. | 0.036° Bé. 0.00034 sp. gr. | 0.065° Bé. 0.00061 sp. gr. |
| 30° Bé. | 0.035° Bé. 0.00039 sp. gr. | 0.063° Bé. 0.00070 sp. gr. |
| 40° Bé. | 0.031° Bé. 0.00041 sp. gr. | 0.056° Bé. 0.00074 sp. gr. |
| 50° Bé. | 0.028° Bé. 0.00045 sp. gr. | 0.050° Bé. 0.00081 sp. gr. |
| 60° Bé. | 0.026° Bé. 0.00053 sp. gr. | 0.047° Bé. 0.00095 sp. gr. |
| 63° Bé. | 0.026° Bé. 0.00057 sp. gr. | 0.047° Bé. 0.00103 sp. gr. |
| 66° Bé. | 0.0235° Bé. 0.00054 sp. gr. | 0.042° Bé. 0.00097 sp. gr. |
| 94% H ₂ SO ₄ | 0.00054 sp. gr. | 0.00097 sp. gr. |
| 98% H ₂ SO ₄ | 0.00053 sp. gr. | 0.00095 sp. gr. |
| 97½% H ₂ SO ₄ | 0.00052 sp. gr. | 0.00094 sp. gr. |
| 100% H ₂ SO ₄ | 0.00052 sp. gr. | 0.00094 sp. gr. |

APPROXIMATE BOILING POINTS

| Degrees Baumé | Boiling Point |
|---------------|---------------|
| | ° F. |
| 50 | 205 |
| 60 | 386 |
| 61 | 400 |
| 62 | 415 |
| 63 | 432 |
| 64 | 451 |
| 65 | 485 |
| 66 | 538 |
| | ° C. |
| | 146.1 |
| | 196.7 |
| | 204.4 |
| | 212.8 |
| | 222.2 |
| | 232.8 |
| | 251.0 |
| | 281.1 |

TABLE LXXXIX.—SULFURIC ACID

By G. LUNGE AND M. ISLER
(Zts. ang. Chem. 1890, 3, 433)

| Specific Gravity 15°/4° in Vacuo | 100 Parts by Weight Correspond to % SO ₄ H ₂ SO ₄ | 1 Liter Contains Grams SO ₄ H ₂ SO ₄ | Specific Gravity 15°/4° in Vacuo | 100 Parts by Weight Correspond to % SO ₄ H ₂ SO ₄ | 1 Liter Contains Grams SO ₄ H ₂ SO ₄ |
|--|---|--|--|---|--|
| 1.000 | 0.07 0.09 | 1 | 1.345 | 36.14 44.28 | 486 596 |
| 1.005 | 0.68 0.83 | 7 | 1.350 | 36.58 44.82 | 494 605 |
| 1.010 | 1.28 1.57 | 13 | 1.355 | 37.02 45.35 | 502 614 |
| 1.015 | 1.88 2.30 | 19 | 1.360 | 37.45 45.88 | 509 624 |
| 1.020 | 2.47 3.03 | 25 | 1.365 | 37.89 46.41 | 517 633 |
| 1.025 | 3.07 3.76 | 32 | 1.370 | 38.32 46.94 | 525 643 |
| 1.030 | 3.67 4.49 | 38 | 1.375 | 38.75 47.47 | 533 653 |
| 1.035 | 4.27 5.23 | 44 | 1.380 | 39.18 48.00 | 541 662 |
| 1.040 | 4.87 5.96 | 51 | 1.385 | 39.62 48.53 | 549 672 |
| 1.045 | 5.45 6.67 | 57 | 1.390 | 40.05 49.06 | 557 682 |
| 1.050 | 6.02 7.37 | 63 | 1.395 | 40.48 49.59 | 564 692 |
| 1.055 | 6.59 8.07 | 70 | 1.400 | 40.91 50.11 | 573 702 |
| 1.060 | 7.16 8.77 | 76 | 1.405 | 41.33 50.63 | 581 711 |
| 1.065 | 7.73 9.47 | 82 | 1.410 | 41.76 51.15 | 589 721 |
| 1.070 | 8.32 10.19 | 89 | 1.415 | 42.17 51.66 | 597 730 |
| 1.075 | 8.90 10.90 | 96 | 1.420 | 42.57 52.15 | 604 740 |
| 1.080 | 9.47 11.60 | 103 | 1.425 | 42.96 52.63 | 612 750 |
| 1.085 | 10.04 12.30 | 109 | 1.430 | 43.36 53.11 | 620 759 |
| 1.090 | 10.60 12.99 | 116 | 1.435 | 43.75 53.59 | 628 769 |
| 1.095 | 11.16 13.67 | 122 | 1.440 | 44.14 54.07 | 636 779 |
| 1.100 | 11.71 14.35 | 129 | 1.445 | 44.53 54.55 | 643 789 |
| 1.105 | 12.27 15.03 | 136 | 1.450 | 44.92 55.03 | 651 798 |
| 1.110 | 12.82 15.71 | 143 | 1.455 | 45.31 55.50 | 659 808 |
| 1.115 | 13.36 16.36 | 149 | 1.460 | 45.69 55.97 | 667 817 |
| 1.120 | 13.89 17.01 | 156 | 1.465 | 46.07 56.43 | 675 827 |
| 1.125 | 14.42 17.66 | 162 | 1.470 | 46.45 56.90 | 683 837 |
| 1.130 | 14.95 18.31 | 169 | 1.475 | 46.83 57.37 | 691 846 |
| 1.135 | 15.48 18.96 | 176 | 1.480 | 47.21 57.83 | 699 856 |
| 1.140 | 16.01 19.61 | 183 | 1.485 | 47.57 58.28 | 707 865 |
| 1.145 | 16.54 20.26 | 189 | 1.490 | 47.95 58.74 | 715 876 |
| 1.150 | 17.07 20.91 | 196 | 1.495 | 48.34 59.22 | 723 885 |
| 1.155 | 17.59 21.55 | 203 | 1.500 | 48.73 59.70 | 731 896 |
| 1.160 | 18.11 22.19 | 210 | 1.505 | 49.12 60.18 | 739 906 |
| 1.165 | 18.64 22.83 | 217 | 1.510 | 49.51 60.65 | 748 916 |
| 1.170 | 19.16 23.47 | 224 | 1.515 | 49.90 61.12 | 756 926 |
| 1.175 | 19.69 24.12 | 231 | 1.520 | 50.28 61.59 | 764 936 |
| 1.180 | 20.21 24.76 | 238 | 1.525 | 50.66 62.06 | 773 946 |
| 1.185 | 20.73 25.40 | 246 | 1.530 | 51.04 62.53 | 781 957 |
| 1.190 | 21.26 26.04 | 253 | 1.535 | 51.43 63.00 | 789 967 |
| 1.195 | 21.78 26.68 | 260 | 1.540 | 51.78 63.43 | 797 977 |
| 1.200 | 22.30 27.32 | 268 | 1.545 | 52.12 63.85 | 805 987 |
| 1.205 | 22.82 27.95 | 275 | 1.550 | 52.46 64.26 | 813 996 |
| 1.210 | 23.33 28.58 | 282 | 1.555 | 52.79 64.67 | 821 1006 |
| 1.215 | 23.84 29.21 | 290 | 1.560 | 53.12 65.08 | 829 1015 |
| 1.220 | 24.36 29.84 | 297 | 1.565 | 53.46 65.49 | 837 1025 |
| 1.225 | 24.88 30.48 | 305 | 1.570 | 53.80 65.90 | 845 1035 |
| 1.230 | 25.39 31.11 | 312 | 1.575 | 54.13 66.30 | 853 1044 |
| 1.235 | 25.88 31.70 | 320 | 1.580 | 54.46 66.71 | 861 1054 |
| 1.240 | 26.35 32.28 | 327 | 1.585 | 54.80 67.13 | 869 1064 |
| 1.245 | 26.83 32.86 | 334 | 1.590 | 55.18 67.59 | 877 1073 |
| 1.250 | 27.29 33.43 | 341 | 1.595 | 55.55 68.05 | 886 1085 |
| 1.255 | 27.76 34.00 | 348 | 1.600 | 55.93 68.51 | 894 1096 |
| 1.260 | 28.22 34.57 | 356 | 1.605 | 56.30 68.97 | 904 1107 |
| 1.265 | 28.69 35.14 | 363 | 1.610 | 56.68 69.43 | 913 1118 |
| 1.270 | 29.15 35.71 | 370 | 1.615 | 57.05 69.89 | 921 1128 |
| 1.275 | 29.62 36.29 | 377 | 1.620 | 57.40 70.32 | 930 1138 |
| 1.280 | 30.10 36.87 | 385 | 1.625 | 57.75 70.74 | 938 1150 |
| 1.285 | 30.57 37.45 | 393 | 1.630 | 58.09 71.16 | 947 1160 |
| 1.290 | 31.04 38.03 | 400 | 1.635 | 58.43 71.57 | 955 1170 |
| 1.295 | 31.52 38.61 | 408 | 1.640 | 58.77 71.99 | 964 1181 |
| 1.300 | 31.99 39.19 | 416 | 1.645 | 59.10 72.40 | 972 1192 |
| 1.305 | 32.46 39.77 | 424 | 1.650 | 59.45 72.82 | 981 1202 |
| 1.310 | 32.94 40.35 | 432 | 1.655 | 59.78 73.23 | 989 1212 |
| 1.315 | 33.41 40.93 | 439 | 1.660 | 60.11 73.64 | 998 1222 |
| 1.320 | 33.88 41.50 | 447 | 1.665 | 60.46 74.07 | 1007 1233 |
| 1.325 | 34.35 42.08 | 455 | 1.670 | 60.82 74.51 | 1016 1244 |
| 1.330 | 34.80 42.66 | 462 | 1.675 | 61.20 74.97 | 1025 1256 |
| 1.335 | 35.27 43.20 | 471 | 1.680 | 61.57 75.42 | 1034 1267 |
| 1.340 | 35.71 43.74 | 479 | 1.685 | 61.93 75.86 | 1043 1278 |

TABLE LXXXIX. (Concluded)

| Specific Gravity 15°/4° in Vacuo | 100 Parts by Weight Correspond to | | 1 Liter Contains | | Specific Gravity 15°/4° in Vacuo | 100 Parts by Weight Correspond to | | 1 Liter Contains | |
|--|--------------------------------------|--------------------------------|---------------------|--------------------------------|--|--------------------------------------|--------------------------------|---------------------|--------------------------------|
| | SO ₃ | H ₂ SO ₄ | SO ₃ | H ₂ SO ₄ | | SO ₃ | H ₂ SO ₄ | SO ₃ | H ₂ SO ₄ |
| 1.690 | 62.29 | 76.30 | 1053 | 1289 | 1.822 | 73.80 | 90.40 | 1345 | 1647 |
| 1.695 | 62.64 | 76.73 | 1062 | 1301 | 1.823 | 73.96 | 90.60 | 1348 | 1651 |
| 1.700 | 63.00 | 77.17 | 1071 | 1312 | 1.824 | 74.12 | 90.80 | 1352 | 1656 |
| 1.705 | 63.35 | 77.60 | 1080 | 1323 | 1.825 | 74.29 | 91.00 | 1356 | 1661 |
| 1.710 | 63.70 | 78.04 | 1089 | 1334 | 1.826 | 74.49 | 91.25 | 1360 | 1666 |
| 1.715 | 64.07 | 78.48 | 1099 | 1346 | 1.827 | 74.69 | 91.50 | 1364 | 1671 |
| 1.720 | 64.43 | 78.92 | 1108 | 1357 | 1.828 | 74.86 | 91.70 | 1368 | 1676 |
| 1.725 | 64.78 | 79.36 | 1118 | 1369 | 1.829 | 75.03 | 91.90 | 1372 | 1681 |
| 1.730 | 65.14 | 79.80 | 1127 | 1381 | 1.830 | 75.19 | 92.10 | 1376 | 1685 |
| 1.735 | 65.50 | 80.24 | 1136 | 1392 | 1.831 | 75.35 | 92.30 | 1380 | 1690 |
| 1.740 | 65.86 | 80.68 | 1146 | 1404 | 1.832 | 75.53 | 92.52 | 1384 | 1695 |
| 1.745 | 66.22 | 81.12 | 1156 | 1416 | 1.833 | 75.72 | 92.75 | 1388 | 1700 |
| 1.750 | 66.58 | 81.56 | 1165 | 1427 | 1.834 | 75.96 | 93.05 | 1393 | 1706 |
| 1.755 | 66.94 | 82.00 | 1175 | 1439 | 1.835 | 76.27 | 93.43 | 1400 | 1713 |
| 1.760 | 67.30 | 82.44 | 1185 | 1451 | 1.836 | 76.57 | 93.80 | 1405 | 1722 |
| 1.765 | 67.65 | 82.88 | 1194 | 1463 | 1.837 | 76.90 | 94.20 | 1412 | 1730 |
| 1.770 | 68.02 | 83.32 | 1204 | 1475 | 1.838 | 77.23 | 94.60 | 1419 | 1739 |
| 1.775 | 68.40 | 83.90 | 1216 | 1489 | 1.839 | 77.55 | 95.00 | 1426 | 1748 |
| 1.780 | 68.98 | 84.50 | 1228 | 1504 | 1.840 | 78.04 | 95.60 | 1436 | 1759 |
| 1.785 | 69.47 | 85.10 | 1240 | 1519 | 1.8405 | 78.33 | 95.95 | 1441 | 1765 |
| 1.790 | 69.96 | 85.70 | 1252 | 1534 | 1.8410 | 79.19 | 97.00 | 1458 | 1786 |
| 1.795 | 70.46 | 86.30 | 1265 | 1549 | 1.8415 | 79.76 | 97.70 | 1469 | 1799 |
| 1.800 | 70.94 | 86.90 | 1277 | 1564 | 1.8410 | 80.16 | 98.20 | 1476 | 1808 |
| 1.805 | 71.50 | 87.60 | 1291 | 1581 | 1.8405 | 80.57 | 98.70 | 1483 | 1816 |
| 1.810 | 72.08 | 88.30 | 1305 | 1598 | 1.8400 | 80.98 | 99.20 | 1490 | 1825 |
| 1.815 | 72.69 | 89.05 | 1319 | 1621 | 1.8395 | 81.18 | 99.45 | 1494 | 1830 |
| 1.820 | 73.51 | 90.05 | 1338 | 1639 | 1.8390 | 81.39 | 99.70 | 1497 | 1834 |
| 1.821 | 73.63 | 90.20 | 1341 | 1643 | 1.8385 | 81.59 | 99.95 | 1500 | 1838 |

TABLE XC.—TEMPERATURE CORRECTIONS TO PER CENT. OF SULFURIC ACID DETERMINED BY HYDROMETER (STANDARD AT 20° C.)

(Calculated from the same data as the preceding table, assuming Jena 16¹¹¹ glass the material used. The table should be used with caution, and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air.)

| Observed Per cent. H ₂ SO ₄ | Temperature in Degrees Centigrade | | | | | | | | | |
|---|-------------------------------------|------|------|------|------|---------------------------|------|------|------|------|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 |
| | Subtract from Observed Per cent. | | | | | Add to Observed Per cent. | | | | |
| 0 | | | | | | 0.16 | 0.35 | 0.59 | 0.86 | 1.17 |
| 5 | 0.59 | 0.49 | 0.36 | 0.20 | 0.24 | 0.50 | 0.79 | 1.11 | 1.45 | 1.8 |
| 10 | 0.92 | 0.72 | 0.51 | 0.27 | 0.29 | 0.60 | 0.93 | 1.28 | 1.65 | 2.0 |
| 20 | 1.39 | 1.06 | 0.72 | 0.36 | 0.37 | 0.75 | 1.14 | 1.53 | 1.93 | 2.3 |
| 30 | 1.64 | 1.23 | 0.82 | 0.41 | 0.41 | 0.82 | 1.24 | 1.65 | 2.07 | 2.5 |
| 40 | 1.65 | 1.24 | 0.82 | 0.41 | 0.41 | 0.82 | 1.22 | 1.62 | 2.03 | 2.4 |
| 50 | 1.56 | 1.17 | 0.78 | 0.39 | 0.38 | 0.77 | 1.15 | 1.52 | 1.90 | 2.3 |
| 60 | 1.52 | 1.14 | 0.76 | 0.38 | 0.37 | 0.74 | 1.11 | 1.48 | 1.84 | 2.2 |
| 70 | 1.54 | 1.15 | 0.76 | 0.38 | 0.38 | 0.75 | 1.13 | 1.50 | 1.86 | 2.2 |
| 80 | 1.72 | 1.30 | 0.87 | 0.44 | 0.45 | 0.90 | 1.36 | 1.83 | 2.31 | 2.8 |
| 81 | 1.76 | 1.34 | 0.92 | 0.44 | 0.47 | 0.93 | 1.42 | 1.93 | 2.44 | 3.0 |
| 82 | 1.84 | 1.41 | 0.96 | 0.47 | 0.50 | 1.00 | 1.51 | 2.04 | 2.58 | 3.1 |
| 83 | 1.94 | 1.48 | 1.00 | 0.50 | 0.53 | 1.06 | 1.59 | 2.18 | 2.78 | 3.4 |
| 84 | 2.05 | 1.57 | 1.06 | 0.53 | 0.55 | 1.12 | 1.74 | 2.36 | 3.0 | 3.7 |
| 85 | 2.20 | 1.67 | 1.13 | 0.57 | 0.61 | 1.23 | 1.88 | 2.57 | 3.3 | 4.0 |
| 86 | 2.36 | 1.80 | 1.22 | 0.62 | 0.66 | 1.35 | 2.08 | 2.84 | 3.7 | 4.6 |
| 87 | 2.54 | 1.95 | 1.32 | 0.67 | 0.73 | 1.50 | 2.31 | 3.2 | 4.1 | 5.2 |
| 88 | 2.75 | 2.12 | 1.44 | 0.74 | 0.81 | 1.67 | 2.59 | 3.6 | 4.7 | 6.0 |
| 89 | 3.01 | 2.31 | 1.58 | 0.82 | 0.89 | 1.86 | 2.91 | 4.1 | 5.6 | ... |
| 90 | 3.27 | 2.53 | 1.73 | 0.91 | 0.99 | 2.10 | 3.4 | 4.9 | ... | ... |
| 91 | 3.57 | 2.78 | 1.93 | 1.01 | 1.13 | 2.44 | 4.1 | ... | ... | ... |
| 92 | 3.91 | 3.08 | 2.13 | 1.12 | 1.32 | 3.00 | ... | ... | ... | ... |
| 93 | 4.29 | 3.38 | 2.37 | 1.26 | 1.64 | ... | ... | ... | ... | ... |
| 94 | 4.75 | 3.77 | 2.69 | 1.46 | ... | ... | ... | ... | ... | ... |
| 95 | 5.29 | 4.26 | 3.12 | 1.76 | ... | ... | ... | ... | ... | ... |
| 96 | 5.96 | 4.88 | 3.65 | 2.19 | ... | ... | ... | ... | ... | ... |
| 97 | 6.78 | 5.68 | 4.42 | 2.80 | ... | ... | ... | ... | ... | ... |

TABLE XCI.—SHOWING THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC GRAVITY OF SULFURIC ACID

a, Specific gravity at 15°/4°; under *t*, changes in specific gravity at the temperature *t*

| a | <i>t</i> 0° | <i>t</i> 10° | <i>t</i> 20° | <i>t</i> 30° | <i>t</i> 40° | <i>t</i> 50° | <i>t</i> 60° |
|-------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.840 | +0.015 | +0.005 | —0.005 | —0.015 | —0.025 | —0.034 | —0.044 |
| 1.820 | 16 | 5 | 5 | 16 | 26 | 37 | 47 |
| 1.800 | 17 | 5 | 5 | 16 | 27 | 37 | 47 |
| 1.780 | 17 | 5 | 5 | 16 | 27 | 37 | 47 |
| 1.760 | 16 | 5 | 5 | 16 | 26 | 36 | 47 |
| 1.740 | 16 | 5 | 5 | 15 | 25 | 35 | 45 |
| 1.720 | 15 | 5 | 5 | 15 | 25 | 35 | 44 |
| 1.700 | 15 | 5 | 5 | 14 | 24 | 33 | 43 |
| 1.680 | 15 | 5 | 5 | 14 | 24 | 33 | 42 |
| 1.660 | 14 | 5 | 5 | 14 | 23 | 32 | 41 |
| 1.640 | 14 | 5 | 4 | 14 | 23 | 32 | 40 |
| 1.620 | 14 | 4 | 4 | 14 | 22 | 31 | 40 |
| 1.600 | 14 | 4 | 4 | 13 | 22 | 31 | 39 |
| 1.580 | 14 | 4 | 4 | 13 | 22 | 30 | 39 |
| 1.560 | 13 | 4 | 4 | 13 | 21 | 30 | 38 |
| 1.540 | 13 | 4 | 4 | 13 | 21 | 30 | 38 |
| 1.520 | 13 | 4 | 4 | 13 | 21 | 29 | 37 |
| 1.500 | 13 | 4 | 4 | 12 | 21 | 29 | 37 |
| 1.480 | 13 | 4 | 4 | 12 | 20 | 28 | 36 |
| 1.460 | 12 | 4 | 4 | 12 | 20 | 28 | 36 |
| 1.440 | 12 | 4 | 4 | 12 | 20 | 28 | 35 |
| 1.420 | 12 | 4 | 4 | 12 | 19 | 27 | 35 |
| 1.400 | 12 | 4 | 4 | 12 | 19 | 27 | 34 |
| 1.380 | 12 | 4 | 4 | 11 | 19 | 27 | 34 |
| 1.360 | 11 | 4 | 4 | 11 | 19 | 26 | 34 |
| 1.340 | 11 | 4 | 4 | 11 | 19 | 26 | 33 |
| 1.320 | 11 | 3 | 4 | 11 | 18 | 26 | 33 |
| 1.300 | 11 | 3 | 3 | 11 | 18 | 25 | 33 |
| 1.280 | 11 | 3 | 3 | 11 | 18 | 25 | 32 |
| 1.260 | 11 | 3 | 3 | 10 | 18 | 24 | 32 |
| 1.240 | 11 | 3 | 3 | 10 | 17 | 24 | 31 |
| 1.220 | 10 | 3 | 3 | 10 | 17 | 23 | 30 |
| 1.200 | 10 | 3 | 3 | 10 | 16 | 23 | 29 |
| 1.180 | 10 | 3 | 3 | 9 | 15 | 22 | 28 |
| 1.160 | 9 | 3 | 3 | 9 | 14 | 20 | 27 |
| 1.140 | 8 | 3 | 3 | 8 | 14 | 19 | 26 |
| 1.120 | 7 | 2 | 2 | 7 | 13 | 18 | 25 |
| 1.100 | 7 | 2 | 2 | 7 | 12 | 17 | 24 |
| 1.080 | 6 | 2 | 2 | 6 | 10 | 16 | 23 |
| 1.060 | 5 | 2 | 2 | 5 | 9 | 14 | 21 |
| 1.040 | 3 | 1 | 1 | 4 | 8 | 13 | 19 |
| 1.020 | 2 | 1 | 1 | 4 | 7 | 12 | 17 |
| 1.010 | 2 | 1 | 1 | 4 | 7 | 12 | 17 |

For temperatures below 15° the values given in the column *t* must, of course, be subtracted from the observed reading; for temperature above 15° the corrections must be added to give the value at 15°. A table has also been calculated by Fuchs (Z. angew. Chem. 1898, II, 950) for this correction.

TABLE XCII.—TEMPERATURE CORRECTION TABLE FOR SULFURIC ACID
 CORRECTING BAUMÉ READINGS AT DIFFERENT TEMPERATURES TO BASIS OF 80 DEGREES FAHRENHEIT
 EXAMPLE.—Acid testing 49° B_e at 150° F. from tables is equivalent to 51.5° B_e at 80° F.

| Baumé | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 170° | 180° | 190° | 200° | 250° |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. | F. |
| 40..... | 40.1 | 40.4 | 40.7 | 41.0 | 41.3 | 41.6 | 41.9 | 42.2 | 42.5 | 42.8 | 43.1 | 43.4 | 43.7 | 44.0 | 44.3 | 44.6 | 44.9 | 45.2 | 45.5 |
| 41..... | 41.1 | 41.4 | 41.7 | 42.0 | 42.3 | 42.6 | 42.9 | 43.2 | 43.5 | 43.8 | 44.1 | 44.4 | 44.7 | 45.0 | 45.3 | 45.6 | 45.9 | 46.2 | 46.5 |
| 42..... | 42.1 | 42.4 | 42.7 | 43.0 | 43.3 | 43.6 | 43.9 | 44.2 | 44.5 | 44.8 | 45.1 | 45.4 | 45.7 | 46.0 | 46.3 | 46.6 | 46.9 | 47.2 | 47.5 |
| 43..... | 43.1 | 43.4 | 43.7 | 44.0 | 44.3 | 44.6 | 44.9 | 45.2 | 45.5 | 45.8 | 46.1 | 46.4 | 46.7 | 47.0 | 47.3 | 47.6 | 47.9 | 48.2 | 48.5 |
| 44..... | 44.1 | 44.4 | 44.7 | 45.0 | 45.3 | 45.6 | 45.9 | 46.2 | 46.5 | 46.8 | 47.1 | 47.4 | 47.7 | 48.0 | 48.3 | 48.6 | 48.9 | 49.2 | 49.5 |
| 45..... | 45.1 | 45.4 | 45.7 | 46.0 | 46.3 | 46.6 | 46.9 | 47.2 | 47.5 | 47.8 | 48.1 | 48.4 | 48.7 | 49.0 | 49.3 | 49.6 | 49.9 | 50.2 | 50.5 |
| 46..... | 46.1 | 46.4 | 46.7 | 47.0 | 47.3 | 47.6 | 47.9 | 48.2 | 48.5 | 48.8 | 49.1 | 49.4 | 49.7 | 50.0 | 50.3 | 50.6 | 50.9 | 51.2 | 51.5 |
| 47..... | 47.1 | 47.4 | 47.7 | 48.0 | 48.3 | 48.6 | 48.9 | 49.2 | 49.5 | 49.8 | 50.1 | 50.4 | 50.7 | 51.0 | 51.3 | 51.6 | 51.9 | 52.2 | 52.5 |
| 48..... | 48.1 | 48.4 | 48.7 | 49.0 | 49.3 | 49.6 | 49.9 | 50.2 | 50.5 | 50.8 | 51.1 | 51.4 | 51.7 | 52.0 | 52.3 | 52.6 | 52.9 | 53.2 | 53.5 |
| 49..... | 49.1 | 49.4 | 49.7 | 50.0 | 50.3 | 50.6 | 50.9 | 51.2 | 51.5 | 51.8 | 52.1 | 52.4 | 52.7 | 53.0 | 53.3 | 53.6 | 53.9 | 54.2 | 54.5 |
| 50..... | 50.1 | 50.4 | 50.7 | 51.0 | 51.3 | 51.6 | 51.9 | 52.2 | 52.5 | 52.8 | 53.1 | 53.4 | 53.7 | 54.0 | 54.3 | 54.6 | 54.9 | 55.2 | 55.5 |
| 51..... | 51.1 | 51.4 | 51.7 | 52.0 | 52.3 | 52.6 | 52.9 | 53.2 | 53.5 | 53.8 | 54.1 | 54.4 | 54.7 | 55.0 | 55.3 | 55.6 | 55.9 | 56.2 | 56.5 |
| 52..... | 52.1 | 52.4 | 52.7 | 53.0 | 53.3 | 53.6 | 53.9 | 54.2 | 54.5 | 54.8 | 55.1 | 55.4 | 55.7 | 56.0 | 56.3 | 56.6 | 56.9 | 57.2 | 57.5 |
| 53..... | 53.1 | 53.4 | 53.7 | 54.0 | 54.3 | 54.6 | 54.9 | 55.2 | 55.5 | 55.8 | 56.1 | 56.4 | 56.7 | 57.0 | 57.3 | 57.6 | 57.9 | 58.2 | 58.5 |
| 54..... | 54.1 | 54.4 | 54.7 | 55.0 | 55.3 | 55.6 | 55.9 | 56.2 | 56.5 | 56.8 | 57.1 | 57.4 | 57.7 | 58.0 | 58.3 | 58.6 | 58.9 | 59.2 | 59.5 |
| 55..... | 55.1 | 55.4 | 55.7 | 56.0 | 56.3 | 56.6 | 56.9 | 57.2 | 57.5 | 57.8 | 58.1 | 58.4 | 58.7 | 59.0 | 59.3 | 59.6 | 59.9 | 60.2 | 60.5 |
| 56..... | 56.1 | 56.4 | 56.7 | 57.0 | 57.3 | 57.6 | 57.9 | 58.2 | 58.5 | 58.8 | 59.1 | 59.4 | 59.7 | 60.0 | 60.3 | 60.6 | 60.9 | 61.2 | 61.5 |
| 57..... | 57.1 | 57.4 | 57.7 | 58.0 | 58.3 | 58.6 | 58.9 | 59.2 | 59.5 | 59.8 | 60.1 | 60.4 | 60.7 | 61.0 | 61.3 | 61.6 | 61.9 | 62.2 | 62.5 |
| 58..... | 58.1 | 58.4 | 58.7 | 59.0 | 59.3 | 59.6 | 59.9 | 60.2 | 60.5 | 60.8 | 61.1 | 61.4 | 61.7 | 62.0 | 62.3 | 62.6 | 62.9 | 63.2 | 63.5 |
| 59..... | 59.1 | 59.4 | 59.7 | 60.0 | 60.3 | 60.6 | 60.9 | 61.2 | 61.5 | 61.8 | 62.1 | 62.4 | 62.7 | 63.0 | 63.3 | 63.6 | 63.9 | 64.2 | 64.5 |
| 60..... | 60.1 | 60.4 | 60.7 | 61.0 | 61.3 | 61.6 | 61.9 | 62.2 | 62.5 | 62.8 | 63.1 | 63.4 | 63.7 | 64.0 | 64.3 | 64.6 | 64.9 | 65.2 | 65.5 |
| 61..... | 61.1 | 61.4 | 61.7 | 62.0 | 62.3 | 62.6 | 62.9 | 63.2 | 63.5 | 63.8 | 64.1 | 64.4 | 64.7 | 65.0 | 65.3 | 65.6 | 65.9 | 66.2 | 66.5 |
| 62..... | 62.1 | 62.4 | 62.7 | 63.0 | 63.3 | 63.6 | 63.9 | 64.2 | 64.5 | 64.8 | 65.1 | 65.4 | 65.7 | 66.0 | 66.3 | 66.6 | 66.9 | 67.2 | 67.5 |
| 63..... | 63.1 | 63.4 | 63.7 | 64.0 | 64.3 | 64.6 | 64.9 | 65.2 | 65.5 | 65.8 | 66.1 | 66.4 | 66.7 | 67.0 | 67.3 | 67.6 | 67.9 | 68.2 | 68.5 |
| 64..... | 64.1 | 64.4 | 64.7 | 65.0 | 65.3 | 65.6 | 65.9 | 66.2 | 66.5 | 66.8 | 67.1 | 67.4 | 67.7 | 68.0 | 68.3 | 68.6 | 68.9 | 69.2 | 69.5 |
| 65..... | 65.1 | 65.4 | 65.7 | 66.0 | 66.3 | 66.6 | 66.9 | 67.2 | 67.5 | 67.8 | 68.1 | 68.4 | 68.7 | 69.0 | 69.3 | 69.6 | 69.9 | 70.2 | 70.5 |
| 66..... | 66.1 | 66.4 | 66.7 | 67.0 | 67.3 | 67.6 | 67.9 | 68.2 | 68.5 | 68.8 | 69.1 | 69.4 | 69.7 | 70.0 | 70.3 | 70.6 | 70.9 | 71.2 | 71.5 |

TABLE XXIII.—THE THERMAL PROPERTIES OF SULFURIC ACID AND WATER MIXTURES

| % SO ₃ | 20° | 40° | 60° | 80° | 100° | 120° | 140° | 160° | 180° | 200° | 220° | 240° |
|----------------------|---|------|------|------|------|------|------|------|------|------|------|------|
| | VI. Heat of Total Evaporation, Degrees C. | | | | | | | | | | | |
| 40 | 1337 | 1333 | 1330 | 1326 | 1321 | 1315 | 1307 | 1300 | 1288 | 1273 | 1257 | 1239 |
| 41 | 1294 | 1292 | 1289 | 1286 | 1283 | 1280 | 1274 | 1267 | 1251 | 1237 | 1223 | 1207 |
| 42 | 1255 | 1254 | 1252 | 1250 | 1247 | 1244 | 1238 | 1233 | 1219 | 1207 | 1194 | 1180 |
| 43 | 1218 | 1218 | 1216 | 1214 | 1212 | 1209 | 1204 | 1199 | 1187 | 1176 | 1164 | 1152 |
| 44 | 1184 | 1184 | 1182 | 1181 | 1179 | 1177 | 1173 | 1169 | 1158 | 1149 | 1138 | 1127 |
| 45 | 1151 | 1152 | 1151 | 1150 | 1148 | 1146 | 1143 | 1140 | 1131 | 1124 | 1112 | 1102 |
| 46 | 1121 | 1122 | 1122 | 1121 | 1120 | 1119 | 1117 | 1114 | 1107 | 1100 | 1087 | 1077 |
| 47 | 1090 | 1092 | 1092 | 1092 | 1092 | 1091 | 1090 | 1088 | 1083 | 1076 | 1063 | 1053 |
| 48 | 1062 | 1064 | 1064 | 1064 | 1064 | 1064 | 1064 | 1062 | 1058 | 1052 | 1041 | 1030 |
| 49 | 1035 | 1037 | 1039 | 1039 | 1039 | 1040 | 1040 | 1038 | 1034 | 1029 | 1019 | 1009 |
| 50 | 1009 | 1011 | 1014 | 1015 | 1016 | 1017 | 1017 | 1015 | 1011 | 1006 | 998 | 988 |
| 51 | 984 | 987 | 990 | 992 | 993 | 994 | 994 | 993 | 990 | 986 | 978 | 968 |
| 52 | 960 | 963 | 966 | 968 | 970 | 971 | 972 | 971 | 969 | 965 | 958 | 949 |
| 53 | 936 | 939 | 942 | 945 | 947 | 949 | 950 | 949 | 948 | 945 | 938 | 930 |
| 54 | 912 | 915 | 918 | 921 | 924 | 926 | 928 | 928 | 927 | 925 | 919 | 911 |
| 55 | 888 | 892 | 896 | 899 | 902 | 905 | 907 | 907 | 907 | 905 | 901 | 894 |
| 56 | 866 | 871 | 875 | 879 | 882 | 885 | 887 | 887 | 888 | 886 | 884 | 876 |
| 57 | 844 | 849 | 854 | 859 | 862 | 865 | 867 | 869 | 870 | 868 | 866 | 860 |
| 58 | 823 | 828 | 833 | 838 | 842 | 845 | 848 | 850 | 852 | 851 | 848 | 844 |
| 59 | 802 | 807 | 812 | 817 | 821 | 825 | 829 | 831 | 834 | 834 | 831 | 828 |
| 60 | 781 | 786 | 791 | 796 | 800 | 805 | 810 | 813 | 816 | 816 | 815 | 812 |
| 61 | 761 | 767 | 772 | 777 | 782 | 787 | 792 | 796 | 799 | 799 | 799 | 797 |
| 62 | 742 | 746 | 753 | 759 | 765 | 770 | 774 | 778 | 782 | 783 | 784 | 782 |
| 63 | 723 | 729 | 735 | 741 | 747 | 752 | 757 | 762 | 766 | 767 | 769 | 767 |
| 64 | 704 | 711 | 717 | 724 | 730 | 735 | 740 | 745 | 750 | 753 | 755 | 752 |
| 65 | 685 | 692 | 699 | 706 | 713 | 719 | 723 | 729 | 734 | 738 | 740 | 738 |
| 66 | 667 | 675 | 682 | 689 | 696 | 702 | 706 | 712 | 718 | 723 | 725 | 724 |
| 67 | 649 | 657 | 665 | 672 | 679 | 685 | 690 | 696 | 702 | 708 | 710 | 710 |
| 68 | 631 | 639 | 647 | 655 | 662 | 669 | 674 | 680 | 686 | 692 | 694 | 695 |
| 69 | 614 | 622 | 630 | 638 | 645 | 652 | 657 | 664 | 670 | 676 | 678 | 681 |
| 70 | 597 | 605 | 613 | 621 | 628 | 635 | 641 | 648 | 654 | 660 | 662 | 666 |
| 71 | 580 | 588 | 596 | 604 | 611 | 618 | 625 | 632 | 638 | 644 | 646 | 651 |
| 72 | 563 | 571 | 579 | 587 | 594 | 602 | 609 | 616 | 622 | 628 | 631 | 635 |
| 73 | 546 | 554 | 562 | 570 | 578 | 585 | 592 | 599 | 606 | 612 | 616 | 619 |
| 74 | 529 | 537 | 545 | 554 | 562 | 569 | 575 | 583 | 590 | 596 | 601 | 604 |
| 75 | 512 | 520 | 528 | 537 | 546 | 553 | 560 | 567 | 574 | 580 | 586 | 589 |
| 76 | 495 | 504 | 512 | 521 | 529 | 537 | 544 | 551 | 558 | 564 | 571 | 574 |
| 77 | 478 | 487 | 496 | 505 | 513 | 521 | 528 | 535 | 542 | 548 | 555 | 559 |
| 78 | 461 | 471 | 480 | 488 | 496 | 504 | 512 | 519 | 526 | 532 | 539 | 544 |
| 79 | 444 | 454 | 464 | 472 | 480 | 488 | 496 | 503 | 510 | 516 | 523 | 529 |
| 80 | 428 | 438 | 447 | 456 | 464 | 472 | 480 | 487 | 494 | 500 | 507 | 514 |

To find the heat required to evaporate mixture containing m lb. SO₃ from any one percentage to any other, at constant temperature, subtract the data in this table which relate to these percentages and temperature, and multiply by m .
The result is expressed in lb. C. H. U.'s.

TABLE XCIV.—SULFURIC ACID AND WATER MIXTURES
SAMPLE HEAT AT CONSTANT CONCENTRATION

| % SO ₃ | 20° C. | 40° C. | 60° C. | 80° C. | 100° C. | 120° C. | 140° C. | 160° C. | 180° C. | 200° C. | 220° C. | 240° C. | 2° | 4° | 6° | Differences, °C. | | | | | 16° | 18° | 20° |
|-------------------|--------|--------|--------|--------|---------|---------|---------|---------|---------|---------|---------|---------|----|----|----|------------------|----|----|----|----|-----|-----|-----|
| 33 | 66 | 98 | 131 | 164 | 197 | 230 | 262 | 295 | 328 | 361 | 394 | 394 | 3 | 7 | 10 | 13 | 16 | 20 | 23 | 26 | 29 | 32 | |
| 34 | 67 | 99 | 132 | 165 | 198 | 231 | 263 | 296 | 329 | 362 | 395 | 395 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 35 | 68 | 100 | 133 | 166 | 199 | 232 | 264 | 297 | 330 | 363 | 396 | 396 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 36 | 69 | 101 | 134 | 167 | 200 | 233 | 265 | 298 | 331 | 364 | 397 | 397 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 37 | 70 | 102 | 135 | 168 | 201 | 234 | 266 | 299 | 332 | 365 | 398 | 398 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 38 | 71 | 103 | 136 | 169 | 202 | 235 | 267 | 300 | 333 | 366 | 399 | 399 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 39 | 72 | 104 | 137 | 170 | 203 | 236 | 268 | 301 | 334 | 367 | 400 | 400 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 40 | 73 | 105 | 138 | 171 | 204 | 237 | 269 | 302 | 335 | 368 | 401 | 401 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 41 | 74 | 106 | 139 | 172 | 205 | 238 | 270 | 303 | 336 | 369 | 402 | 402 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 42 | 75 | 107 | 140 | 173 | 206 | 239 | 271 | 304 | 337 | 370 | 403 | 403 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 43 | 76 | 108 | 141 | 174 | 207 | 240 | 272 | 305 | 338 | 371 | 404 | 404 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 44 | 77 | 109 | 142 | 175 | 208 | 241 | 273 | 306 | 339 | 372 | 405 | 405 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 45 | 78 | 110 | 143 | 176 | 209 | 242 | 274 | 307 | 340 | 373 | 406 | 406 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 46 | 79 | 111 | 144 | 177 | 210 | 243 | 275 | 308 | 341 | 374 | 407 | 407 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 47 | 80 | 112 | 145 | 178 | 211 | 244 | 276 | 309 | 342 | 375 | 408 | 408 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 48 | 81 | 113 | 146 | 179 | 212 | 245 | 277 | 310 | 343 | 376 | 409 | 409 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 49 | 82 | 114 | 147 | 180 | 213 | 246 | 278 | 311 | 344 | 377 | 410 | 410 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 50 | 83 | 115 | 148 | 181 | 214 | 247 | 279 | 312 | 345 | 378 | 411 | 411 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 51 | 84 | 116 | 149 | 182 | 215 | 248 | 280 | 313 | 346 | 379 | 412 | 412 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 52 | 85 | 117 | 150 | 183 | 216 | 249 | 281 | 314 | 347 | 380 | 413 | 413 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 53 | 86 | 118 | 151 | 184 | 217 | 250 | 282 | 315 | 348 | 381 | 414 | 414 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 54 | 87 | 119 | 152 | 185 | 218 | 251 | 283 | 316 | 349 | 382 | 415 | 415 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 55 | 88 | 120 | 153 | 186 | 219 | 252 | 284 | 317 | 350 | 383 | 416 | 416 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 56 | 89 | 121 | 154 | 187 | 220 | 253 | 285 | 318 | 351 | 384 | 417 | 417 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 57 | 90 | 122 | 155 | 188 | 221 | 254 | 286 | 319 | 352 | 385 | 418 | 418 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 58 | 91 | 123 | 156 | 189 | 222 | 255 | 287 | 320 | 353 | 386 | 419 | 419 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 59 | 92 | 124 | 157 | 190 | 223 | 256 | 288 | 321 | 354 | 387 | 420 | 420 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 60 | 93 | 125 | 158 | 191 | 224 | 257 | 289 | 322 | 355 | 388 | 421 | 421 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 61 | 94 | 126 | 159 | 192 | 225 | 258 | 290 | 323 | 356 | 389 | 422 | 422 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 62 | 95 | 127 | 160 | 193 | 226 | 259 | 291 | 324 | 357 | 390 | 423 | 423 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 63 | 96 | 128 | 161 | 194 | 227 | 260 | 292 | 325 | 358 | 391 | 424 | 424 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 64 | 97 | 129 | 162 | 195 | 228 | 261 | 293 | 326 | 359 | 392 | 425 | 425 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 65 | 98 | 130 | 163 | 196 | 229 | 262 | 294 | 327 | 360 | 393 | 426 | 426 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 66 | 99 | 131 | 164 | 197 | 230 | 263 | 295 | 328 | 361 | 394 | 427 | 427 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 67 | 100 | 132 | 165 | 198 | 231 | 264 | 296 | 329 | 362 | 395 | 428 | 428 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 68 | 101 | 133 | 166 | 199 | 232 | 265 | 297 | 330 | 363 | 396 | 429 | 429 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 69 | 102 | 134 | 167 | 200 | 233 | 266 | 298 | 331 | 364 | 397 | 430 | 430 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 70 | 103 | 135 | 168 | 201 | 234 | 267 | 299 | 332 | 365 | 398 | 431 | 431 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 71 | 104 | 136 | 169 | 202 | 235 | 268 | 300 | 333 | 366 | 399 | 432 | 432 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 72 | 105 | 137 | 170 | 203 | 236 | 269 | 301 | 334 | 367 | 400 | 433 | 433 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 73 | 106 | 138 | 171 | 204 | 237 | 270 | 302 | 335 | 368 | 401 | 434 | 434 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 74 | 107 | 139 | 172 | 205 | 238 | 271 | 303 | 336 | 369 | 402 | 435 | 435 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 75 | 108 | 140 | 173 | 206 | 239 | 272 | 304 | 337 | 370 | 403 | 436 | 436 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 76 | 109 | 141 | 174 | 207 | 240 | 273 | 305 | 338 | 371 | 404 | 437 | 437 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 77 | 110 | 142 | 175 | 208 | 241 | 274 | 306 | 339 | 372 | 405 | 438 | 438 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 78 | 111 | 143 | 176 | 209 | 242 | 275 | 307 | 340 | 373 | 406 | 439 | 439 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 79 | 112 | 144 | 177 | 210 | 243 | 276 | 308 | 341 | 374 | 407 | 440 | 440 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 80 | 113 | 145 | 178 | 211 | 244 | 277 | 309 | 342 | 375 | 408 | 441 | 441 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 81 | 114 | 146 | 179 | 212 | 245 | 278 | 310 | 343 | 376 | 409 | 442 | 442 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 82 | 115 | 147 | 180 | 213 | 246 | 279 | 311 | 344 | 377 | 410 | 443 | 443 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 83 | 116 | 148 | 181 | 214 | 247 | 280 | 312 | 345 | 378 | 411 | 444 | 444 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 84 | 117 | 149 | 182 | 215 | 248 | 281 | 313 | 346 | 379 | 412 | 445 | 445 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 85 | 118 | 150 | 183 | 216 | 249 | 282 | 314 | 347 | 380 | 413 | 446 | 446 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 86 | 119 | 151 | 184 | 217 | 250 | 283 | 315 | 348 | 381 | 414 | 447 | 447 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 87 | 120 | 152 | 185 | 218 | 251 | 284 | 316 | 349 | 382 | 415 | 448 | 448 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 88 | 121 | 153 | 186 | 219 | 252 | 285 | 317 | 350 | 383 | 416 | 449 | 449 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 89 | 122 | 154 | 187 | 220 | 253 | 286 | 318 | 351 | 384 | 417 | 450 | 450 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 90 | 123 | 155 | 188 | 221 | 254 | 287 | 319 | 352 | 385 | 418 | 451 | 451 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 91 | 124 | 156 | 189 | 222 | 255 | 288 | 320 | 353 | 386 | 419 | 452 | 452 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 92 | 125 | 157 | 190 | 223 | 256 | 289 | 321 | 354 | 387 | 420 | 453 | 453 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 93 | 126 | 158 | 191 | 224 | 257 | 290 | 322 | 355 | 388 | 421 | 454 | 454 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 94 | 127 | 159 | 192 | 225 | 258 | 291 | 323 | 356 | 389 | 422 | 455 | 455 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 95 | 128 | 160 | 193 | 226 | 259 | 292 | 324 | 357 | 390 | 423 | 456 | 456 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 96 | 129 | 161 | 194 | 227 | 260 | 293 | 325 | 358 | 391 | 424 | 457 | 457 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 97 | 130 | 162 | 195 | 228 | 261 | 294 | 326 | 359 | 392 | 425 | 458 | 458 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 98 | 131 | 163 | 196 | 229 | 262 | 295 | 327 | 360 | 393 | 426 | 459 | 459 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 99 | 132 | 164 | 197 | 230 | 263 | 296 | 328 | 361 | 394 | 427 | 460 | 460 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |
| 100 | 133 | 165 | 198 | 231 | 264 | 297 | 329 | 362 | 395 | 428 | 461 | 461 | 3 | 7 | 10 | 13 | 16 | 19 | 22 | 25 | 28 | 31 | |

To obtain the heat in lb. C. H. U.'s required to warm a quantity of acid of given % SO₃ in which the total quantity of SO₃ is in lb. from any temperature to any other temperature, subtract the number which corresponds to the lower temperature from that which corresponds to the higher and multiply by m.

● TABLE XCV.—CORRECTIONS FOR HYDROMETER READINGS

Corrections to be added to readings of a hydrometer standardized, at one temperature to convert them to values standardized at another temperature:

The first column shows Specific Gravity at temperature 60°/60° F.* The other columns show the corrections to be applied to indications of a hydrometer standardized at 60°/60° F. to convert it to the standard temperature shown at top of each column.

To convert indications of hydrometers standardized at other than 60°/60° F., add the difference of the corrections shown. Ex.—Reading of a hydrometer standardized at 20°/4° C. is 1.550; to convert to values standardized at 20°/20° C., add 0.0027 equals 1.5527.

| Specific Gravity 60°/60° F. or 15.56°/15.56° C. | Corrections to Be Added | | | | |
|---|-------------------------|-----------|------------|--------------|------------|
| | 15°/4° C. | 20°/4° C. | 20°/20° C. | 17½°/17½° C. | 25°/25° C. |
| 0.650 | —0.0006 | —0.0007 | +0.0005 | +0.0002 | +0.0012 |
| 0.675 | —0.0006 | —0.0007 | +0.0005 | +0.0002 | +0.0012 |
| 0.700 | —0.0007 | —0.0008 | +0.0005 | +0.0002 | +0.0012 |
| 0.750 | —0.0007 | —0.0008 | +0.0005 | +0.0002 | +0.0013 |
| 0.800 | —0.0007 | —0.0008 | +0.0005 | +0.0002 | +0.0013 |
| 0.825 | —0.0008 | —0.0009 | +0.0006 | +0.0002 | +0.0014 |
| 0.875 | —0.0008 | —0.0009 | +0.0006 | +0.0002 | +0.0015 |
| 0.900 | —0.0009 | —0.0010 | +0.0006 | +0.0002 | +0.0016 |
| 0.925 | —0.0009 | —0.0010 | +0.0007 | +0.0002 | +0.0016 |
| 1.000 | —0.0009 | —0.0011 | +0.0007 | +0.0003 | +0.0017 |
| 1.050 | —0.0010 | —0.0011 | +0.0007 | +0.0003 | +0.0018 |
| 1.075 | —0.0010 | —0.0011 | +0.0007 | +0.0003 | +0.0019 |
| 1.100 | —0.0010 | —0.0012 | +0.0008 | +0.0003 | +0.0019 |
| 1.150 | —0.0011 | —0.0012 | +0.0008 | +0.0003 | +0.0020 |
| 1.200 | —0.0011 | —0.0013 | +0.0008 | +0.0003 | +0.0021 |
| 1.225 | —0.0012 | —0.0013 | +0.0009 | +0.0003 | +0.0021 |
| 1.250 | —0.0012 | —0.0013 | +0.0009 | +0.0004 | +0.0022 |
| 1.300 | —0.0012 | —0.0014 | +0.0009 | +0.0004 | +0.0023 |
| 1.325 | —0.0012 | —0.0014 | +0.0009 | +0.0004 | +0.0024 |
| 1.350 | —0.0013 | —0.0014 | +0.0010 | +0.0004 | +0.0024 |
| 1.375 | —0.0013 | —0.0015 | +0.0010 | +0.0004 | +0.0024 |
| 1.400 | —0.0013 | —0.0015 | +0.0010 | +0.0004 | +0.0025 |
| 1.450 | —0.0014 | —0.0015 | +0.0010 | +0.0004 | +0.0025 |
| 1.475 | —0.0014 | —0.0016 | +0.0010 | +0.0004 | +0.0026 |
| 1.500 | —0.0014 | —0.0016 | +0.0011 | +0.0004 | +0.0026 |
| 1.550 | —0.0015 | —0.0016 | +0.0011 | +0.0004 | +0.0027 |
| 1.575 | —0.0015 | —0.0017 | +0.0011 | +0.0004 | +0.0027 |
| 1.600 | —0.0015 | —0.0017 | +0.0011 | +0.0004 | +0.0028 |
| 1.625 | —0.0015 | —0.0017 | +0.0011 | +0.0005 | +0.0028 |
| 1.650 | —0.0016 | —0.0017 | +0.0012 | +0.0005 | +0.0029 |
| 1.700 | —0.0016 | —0.0018 | +0.0012 | +0.0005 | +0.0030 |
| 1.725 | —0.0016 | —0.0018 | +0.0012 | +0.0005 | +0.0031 |
| 1.775 | —0.0017 | —0.0019 | +0.0012 | +0.0005 | +0.0031 |
| 1.800 | —0.0017 | —0.0019 | +0.0013 | +0.0005 | +0.0032 |
| 1.850 | —0.0017 | —0.0019 | +0.0013 | +0.0005 | +0.0032 |
| 1.900 | —0.0018 | —0.0020 | +0.0013 | +0.0005 | +0.0033 |
| 1.925 | —0.0018 | —0.0020 | +0.0014 | +0.0005 | +0.0033 |
| 1.950 | —0.0018 | —0.0021 | +0.0014 | +0.0005 | +0.0034 |
| 2.000 | —0.0019 | —0.0021 | +0.0014 | +0.0006 | +0.0035 |

* 60°/60° F. means readings taken at 60° F. compared to water at 60° F. as 1.0

NOTE. The numbers in bold-face type refer to the temperature either in degrees Centigrade or Fahrenheit which it is desired to convert into the other scale. If converting from Fahrenheit degrees to Centigrade degrees the equivalent temperature will be found in the left column, while if converting from degrees Centigrade to degrees Fahrenheit, the answer will be found in the column on the right.

| 100 to 2000 | | | | 200 to 3000 | | | | | | | |
|-------------|-------------|------|------|-------------|------|------|-------------|------|------|-------------|------|
| C. | F. | C. | F. | C. | F. | C. | F. | | | | |
| 538 | 1000 | 1832 | 815 | 1500 | 2732 | 1093 | 2000 | 3632 | 1371 | 2500 | 4532 |
| 543 | 1010 | 1850 | 820 | 1510 | 2750 | 1098 | 2010 | 3650 | 1376 | 2510 | 4550 |
| 549 | 1020 | 1868 | 827 | 1520 | 2768 | 1104 | 2020 | 3668 | 1382 | 2520 | 4568 |
| 554 | 1030 | 1886 | 833 | 1530 | 2786 | 1109 | 2030 | 3686 | 1387 | 2530 | 4586 |
| 560 | 1040 | 1904 | 838 | 1540 | 2804 | 1115 | 2040 | 3704 | 1393 | 2540 | 4604 |
| 565 | 1050 | 1922 | 842 | 1550 | 2822 | 1120 | 2050 | 3722 | 1398 | 2550 | 4622 |
| 571 | 1060 | 1940 | 849 | 1560 | 2840 | 1126 | 2060 | 3740 | 1404 | 2560 | 4640 |
| 576 | 1070 | 1958 | 853 | 1570 | 2858 | 1131 | 2070 | 3758 | 1409 | 2570 | 4658 |
| 582 | 1080 | 1976 | 860 | 1580 | 2876 | 1137 | 2080 | 3776 | 1415 | 2580 | 4676 |
| 587 | 1090 | 1994 | 864 | 1590 | 2894 | 1142 | 2090 | 3794 | 1420 | 2590 | 4694 |
| 593 | 1100 | 2012 | 871 | 1600 | 2912 | 1149 | 2100 | 3812 | 1427 | 2600 | 4712 |
| 598 | 1110 | 2030 | 876 | 1610 | 2930 | 1154 | 2110 | 3830 | 1432 | 2610 | 4730 |
| 604 | 1120 | 2048 | 882 | 1620 | 2948 | 1159 | 2120 | 3848 | 1438 | 2620 | 4748 |
| 609 | 1130 | 2066 | 887 | 1630 | 2966 | 1165 | 2130 | 3866 | 1443 | 2630 | 4766 |
| 615 | 1140 | 2084 | 893 | 1640 | 2984 | 1171 | 2140 | 3884 | 1449 | 2640 | 4784 |
| 620 | 1150 | 2102 | 898 | 1650 | 3002 | 1176 | 2150 | 3902 | 1454 | 2650 | 4802 |
| 626 | 1160 | 2120 | 904 | 1660 | 3020 | 1182 | 2160 | 3920 | 1460 | 2660 | 4820 |
| 631 | 1170 | 2138 | 909 | 1670 | 3038 | 1187 | 2170 | 3938 | 1465 | 2670 | 4838 |
| 637 | 1180 | 2156 | 915 | 1680 | 3056 | 1193 | 2180 | 3956 | 1471 | 2680 | 4856 |
| 642 | 1190 | 2174 | 920 | 1690 | 3074 | 1198 | 2190 | 3974 | 1476 | 2690 | 4874 |
| 648 | 1200 | 2192 | 926 | 1700 | 3092 | 1204 | 2200 | 3992 | 1483 | 2700 | 4892 |
| 653 | 1210 | 2210 | 931 | 1710 | 3110 | 1209 | 2210 | 4010 | 1488 | 2710 | 4910 |
| 658 | 1220 | 2228 | 937 | 1720 | 3128 | 1215 | 2220 | 4028 | 1494 | 2720 | 4928 |
| 664 | 1230 | 2246 | 942 | 1730 | 3146 | 1220 | 2230 | 4046 | 1499 | 2730 | 4946 |
| 670 | 1240 | 2264 | 948 | 1740 | 3164 | 1226 | 2240 | 4064 | 1505 | 2740 | 4964 |
| 675 | 1250 | 2282 | 953 | 1750 | 3182 | 1231 | 2250 | 4082 | 1510 | 2750 | 4982 |
| 681 | 1260 | 2300 | 959 | 1760 | 3200 | 1237 | 2260 | 4100 | 1516 | 2760 | 5000 |
| 686 | 1270 | 2318 | 964 | 1770 | 3218 | 1242 | 2270 | 4118 | 1521 | 2770 | 5018 |
| 692 | 1280 | 2336 | 970 | 1780 | 3236 | 1248 | 2280 | 4136 | 1526 | 2780 | 5036 |
| 697 | 1290 | 2354 | 975 | 1790 | 3254 | 1253 | 2290 | 4154 | 1532 | 2790 | 5054 |
| 704 | 1300 | 2372 | 981 | 1800 | 3272 | 1259 | 2300 | 4172 | 1538 | 2800 | 5072 |
| 708 | 1310 | 2390 | 986 | 1810 | 3290 | 1264 | 2310 | 4190 | 1543 | 2810 | 5090 |
| 715 | 1320 | 2408 | 992 | 1820 | 3308 | 1270 | 2320 | 4208 | 1549 | 2820 | 5108 |
| 719 | 1330 | 2426 | 997 | 1830 | 3326 | 1275 | 2330 | 4226 | 1554 | 2830 | 5126 |
| 726 | 1340 | 2444 | 1003 | 1840 | 3344 | 1281 | 2340 | 4244 | 1560 | 2840 | 5144 |
| 734 | 1350 | 2462 | 1008 | 1850 | 3362 | 1286 | 2350 | 4262 | 1565 | 2850 | 5162 |
| 737 | 1360 | 2480 | 1014 | 1860 | 3380 | 1292 | 2360 | 4280 | 1570 | 2860 | 5180 |
| 741 | 1370 | 2498 | 1019 | 1870 | 3398 | 1297 | 2370 | 4298 | 1576 | 2870 | 5198 |
| 748 | 1380 | 2516 | 1025 | 1880 | 3416 | 1303 | 2380 | 4316 | 1582 | 2880 | 5216 |
| 752 | 1390 | 2534 | 1031 | 1890 | 3434 | 1308 | 2390 | 4334 | 1587 | 2890 | 5234 |
| 760 | 1400 | 2552 | 1036 | 1900 | 3452 | 1315 | 2400 | 4352 | 1593 | 2900 | 5252 |
| 765 | 1410 | 2570 | 1041 | 1910 | 3470 | 1320 | 2410 | 4370 | 1598 | 2910 | 5270 |
| 771 | 1420 | 2588 | 1047 | 1920 | 3488 | 1326 | 2420 | 4388 | 1604 | 2920 | 5288 |
| 776 | 1430 | 2606 | 1052 | 1930 | 3506 | 1331 | 2430 | 4406 | 1609 | 2930 | 5306 |
| 782 | 1440 | 2624 | 1058 | 1940 | 3524 | 1337 | 2440 | 4424 | 1615 | 2940 | 5324 |
| 787 | 1450 | 2642 | 1063 | 1950 | 3542 | 1342 | 2450 | 4442 | 1620 | 2950 | 5342 |
| 793 | 1460 | 2660 | 1069 | 1960 | 3560 | 1348 | 2460 | 4460 | 1626 | 2960 | 5360 |
| 797 | 1470 | 2678 | 1074 | 1970 | 3578 | 1353 | 2470 | 4478 | 1631 | 2970 | 5378 |
| 804 | 1480 | 2696 | 1080 | 1980 | 3596 | 1359 | 2480 | 4496 | 1637 | 2980 | 5396 |
| 809 | 1490 | 2714 | 1085 | 1990 | 3614 | 1364 | 2490 | 4514 | 1642 | 2990 | 5414 |
| | | | 1093 | 2000 | 3632 | 1369 | | | 1649 | 3000 | 5432 |

TABLE XCVII.—SPECIFIC GRAVITY TABLES FOR NITRIC ACID AT VARIOUS CONCENTRATIONS DETERMINED AT 15°/4° C.

(LUNGE AND REY: Zts. f. angew. Ch. 1891, p. 168)

| Sp. Gr. 15°/4° | C. Air-free | Degrees Baumé | Degrees Twaddell | 100 Parts by Weight Contain | | | | | 1 Liter Contains Kilograms | | | | |
|-------------------|----------------|------------------|---------------------|-----------------------------|------------------|--------------------|--------------------|------------------------|----------------------------|------------------|--------------------|--------------------|------------------------|
| | | | | NO ₂ | HNO ₃ | Acid of 36° Bé. | Acid of 40° Bé. | Acid of 43 1/2° Bé. | NO ₂ | HNO ₃ | Acid of 36° Bé. | Acid of 40° Bé. | Acid of 43 1/2° Bé. |
| 1.000 | 0.1 | 0 | | 0.08 | 0.10 | 0.19 | 0.16 | 0.10 | 0.001 | 0.001 | 0.002 | 0.002 | 0.001 |
| 1.005 | 0.7 | 1 | | 0.85 | 1.00 | 1.89 | 1.61 | 1.03 | 0.008 | 0.010 | 0.019 | 0.016 | 0.010 |
| 1.010 | 1.4 | 2 | | 1.62 | 1.90 | 3.60 | 3.07 | 1.95 | 0.016 | 0.019 | 0.036 | 0.031 | 0.019 |
| 1.015 | 2.1 | 3 | | 2.39 | 2.80 | 5.30 | 4.52 | 2.87 | 0.024 | 0.028 | 0.053 | 0.045 | 0.029 |
| 1.020 | 2.7 | 4 | | 3.17 | 3.70 | 7.01 | 5.98 | 3.79 | 0.033 | 0.038 | 0.072 | 0.061 | 0.039 |
| 1.025 | 3.4 | 5 | | 3.94 | 4.60 | 8.71 | 7.43 | 4.72 | 0.040 | 0.047 | 0.089 | 0.076 | 0.048 |
| 1.030 | 4.1 | 6 | | 4.71 | 5.50 | 10.42 | 8.88 | 5.64 | 0.049 | 0.057 | 0.108 | 0.092 | 0.058 |
| 1.035 | 4.7 | 7 | | 5.47 | 6.38 | 12.08 | 10.30 | 6.54 | 0.057 | 0.066 | 0.125 | 0.107 | 0.068 |
| 1.040 | 5.4 | 8 | | 6.22 | 7.26 | 13.75 | 11.72 | 7.45 | 0.064 | 0.075 | 0.142 | 0.121 | 0.077 |
| 1.045 | 6.0 | 9 | | 6.97 | 8.13 | 15.40 | 13.13 | 8.34 | 0.073 | 0.085 | 0.161 | 0.137 | 0.087 |
| 1.050 | 6.7 | 10 | | 7.71 | 8.99 | 17.03 | 14.52 | 9.22 | 0.081 | 0.094 | 0.178 | 0.152 | 0.096 |
| 1.055 | 7.4 | 11 | | 8.43 | 9.84 | 18.64 | 15.89 | 10.09 | 0.089 | 0.104 | 0.197 | 0.168 | 0.107 |
| 1.060 | 8.0 | 12 | | 9.15 | 10.68 | 20.23 | 17.25 | 10.95 | 0.097 | 0.113 | 0.214 | 0.182 | 0.116 |
| 1.065 | 8.7 | 13 | | 9.87 | 11.51 | 21.80 | 18.59 | 11.81 | 0.105 | 0.123 | 0.233 | 0.198 | 0.126 |
| 1.070 | 9.4 | 14 | | 10.57 | 12.33 | 23.35 | 19.91 | 12.65 | 0.113 | 0.132 | 0.250 | 0.213 | 0.135 |
| 1.075 | 10.0 | 15 | | 11.27 | 13.15 | 24.91 | 21.24 | 13.49 | 0.121 | 0.141 | 0.267 | 0.228 | 0.145 |
| 1.080 | 10.6 | 16 | | 11.96 | 13.95 | 26.42 | 22.53 | 14.31 | 0.129 | 0.151 | 0.286 | 0.244 | 0.155 |
| 1.085 | 11.2 | 17 | | 12.64 | 14.74 | 27.92 | 23.80 | 15.12 | 0.137 | 0.160 | 0.303 | 0.258 | 0.164 |
| 1.090 | 11.9 | 18 | | 13.31 | 15.53 | 29.41 | 25.08 | 15.93 | 0.145 | 0.169 | 0.320 | 0.273 | 0.173 |
| 1.095 | 12.4 | 19 | | 13.97 | 16.32 | 30.91 | 26.35 | 16.74 | 0.153 | 0.179 | 0.339 | 0.289 | 0.184 |
| 1.100 | 13.0 | 20 | | 14.67 | 17.11 | 32.41 | 27.63 | 17.55 | 0.161 | 0.188 | 0.356 | 0.304 | 0.193 |
| 1.105 | 13.6 | 21 | | 15.34 | 17.89 | 33.89 | 28.89 | 18.35 | 0.170 | 0.198 | 0.375 | 0.320 | 0.203 |
| 1.110 | 14.2 | 22 | | 16.00 | 18.67 | 35.36 | 30.15 | 19.15 | 0.177 | 0.207 | 0.392 | 0.335 | 0.212 |
| 1.115 | 14.9 | 23 | | 16.67 | 19.45 | 36.84 | 31.41 | 19.95 | 0.186 | 0.217 | 0.411 | 0.350 | 0.223 |
| 1.120 | 15.5 | 24 | | 17.34 | 20.23 | 38.31 | 32.67 | 20.75 | 0.195 | 0.227 | 0.430 | 0.366 | 0.233 |
| 1.125 | 16.0 | 25 | | 18.00 | 21.00 | 39.77 | 33.91 | 21.54 | 0.202 | 0.236 | 0.447 | 0.381 | 0.242 |
| 1.130 | 16.5 | 26 | | 18.66 | 21.77 | 41.23 | 35.16 | 22.33 | 0.211 | 0.246 | 0.466 | 0.397 | 0.252 |
| 1.135 | 17.1 | 27 | | 19.32 | 22.54 | 42.69 | 36.40 | 23.12 | 0.219 | 0.256 | 0.485 | 0.413 | 0.263 |
| 1.140 | 17.7 | 28 | | 19.98 | 23.31 | 44.15 | 37.65 | 23.91 | 0.228 | 0.266 | 0.504 | 0.430 | 0.273 |
| 1.145 | 18.3 | 29 | | 20.64 | 24.08 | 45.61 | 38.89 | 24.70 | 0.237 | 0.276 | 0.523 | 0.446 | 0.283 |
| 1.150 | 18.8 | 30 | | 21.29 | 24.84 | 47.05 | 40.12 | 25.48 | 0.245 | 0.286 | 0.542 | 0.462 | 0.293 |
| 1.155 | 19.3 | 31 | | 21.94 | 25.60 | 48.49 | 41.35 | 26.26 | 0.254 | 0.296 | 0.561 | 0.478 | 0.304 |
| 1.160 | 19.8 | 32 | | 22.60 | 26.36 | 49.92 | 42.57 | 27.04 | 0.262 | 0.306 | 0.580 | 0.494 | 0.314 |
| 1.165 | 20.3 | 33 | | 23.25 | 27.12 | 51.36 | 43.80 | 27.82 | 0.271 | 0.316 | 0.598 | 0.510 | 0.324 |
| 1.170 | 20.9 | 34 | | 23.90 | 27.88 | 52.80 | 45.03 | 28.59 | 0.279 | 0.326 | 0.617 | 0.526 | 0.334 |
| 1.175 | 21.4 | 35 | | 24.54 | 28.63 | 54.22 | 46.24 | 29.36 | 0.288 | 0.336 | 0.636 | 0.543 | 0.345 |
| 1.180 | 22.0 | 36 | | 25.18 | 29.38 | 55.64 | 47.45 | 30.13 | 0.297 | 0.347 | 0.657 | 0.560 | 0.356 |
| 1.185 | 22.5 | 37 | | 25.83 | 30.13 | 57.07 | 48.66 | 30.90 | 0.306 | 0.357 | 0.676 | 0.577 | 0.366 |
| 1.190 | 23.0 | 38 | | 26.47 | 30.88 | 58.49 | 49.87 | 31.67 | 0.315 | 0.367 | 0.695 | 0.593 | 0.376 |
| 1.195 | 23.5 | 39 | | 27.10 | 31.62 | 59.89 | 51.07 | 32.43 | 0.324 | 0.378 | 0.715 | 0.610 | 0.388 |
| 1.200 | 24.0 | 40 | | 27.74 | 32.36 | 61.29 | 52.26 | 33.19 | 0.333 | 0.388 | 0.735 | 0.627 | 0.398 |
| 1.205 | 24.5 | 41 | | 28.36 | 33.09 | 62.67 | 53.23 | 33.94 | 0.342 | 0.399 | 0.755 | 0.644 | 0.409 |
| 1.210 | 25.0 | 42 | | 28.99 | 33.82 | 64.05 | 54.21 | 34.69 | 0.351 | 0.409 | 0.775 | 0.661 | 0.419 |
| 1.215 | 25.5 | 43 | | 29.61 | 34.55 | 65.44 | 55.18 | 35.44 | 0.360 | 0.420 | 0.795 | 0.678 | 0.431 |
| 1.220 | 26.0 | 44 | | 30.24 | 35.28 | 66.82 | 56.16 | 36.18 | 0.369 | 0.430 | 0.815 | 0.695 | 0.441 |
| 1.225 | 26.4 | 45 | | 30.88 | 36.03 | 68.24 | 57.14 | 36.95 | 0.378 | 0.441 | 0.835 | 0.712 | 0.452 |
| 1.230 | 26.9 | 46 | | 31.53 | 36.78 | 69.66 | 58.13 | 37.72 | 0.387 | 0.452 | 0.856 | 0.730 | 0.466 |
| 1.235 | 27.4 | 47 | | 32.17 | 37.53 | 71.08 | 60.61 | 38.49 | 0.397 | 0.463 | 0.877 | 0.748 | 0.475 |
| 1.240 | 27.9 | 48 | | 32.82 | 38.29 | 72.52 | 61.84 | 39.27 | 0.407 | 0.475 | 0.900 | 0.767 | 0.487 |
| 1.245 | 28.4 | 49 | | 33.47 | 39.05 | 73.96 | 63.07 | 40.05 | 0.417 | 0.486 | 0.921 | 0.785 | 0.498 |
| 1.250 | 28.8 | 50 | | 34.13 | 39.82 | 75.42 | 64.31 | 40.84 | 0.427 | 0.498 | 0.943 | 0.804 | 0.511 |
| 1.255 | 29.3 | 51 | | 34.78 | 40.58 | 76.86 | 65.54 | 41.62 | 0.437 | 0.509 | 0.965 | 0.822 | 0.522 |
| 1.260 | 29.7 | 52 | | 35.44 | 41.34 | 78.30 | 66.76 | 42.40 | 0.447 | 0.521 | 0.987 | 0.841 | 0.534 |
| 1.265 | 30.2 | 53 | | 36.09 | 42.10 | 79.74 | 67.99 | 43.18 | 0.457 | 0.533 | 1.009 | 0.860 | 0.547 |
| 1.270 | 30.6 | 54 | | 36.75 | 42.87 | 81.23 | 69.23 | 43.97 | 0.467 | 0.544 | 1.031 | 0.879 | 0.558 |
| 1.275 | 31.1 | 55 | | 37.41 | 43.64 | 82.65 | 70.48 | 44.76 | 0.477 | 0.556 | 1.054 | 0.898 | 0.570 |
| 1.280 | 31.5 | 56 | | 38.07 | 44.41 | 84.11 | 71.72 | 45.55 | 0.487 | 0.568 | 1.077 | 0.918 | 0.583 |
| 1.285 | 32.0 | 57 | | 38.73 | 45.18 | 85.57 | 72.96 | 46.34 | 0.498 | 0.581 | 1.100 | 0.938 | 0.596 |
| 1.290 | 32.4 | 58 | | 39.39 | 45.95 | 87.03 | 74.21 | 47.13 | 0.508 | 0.593 | 1.123 | 0.957 | 0.608 |
| 1.295 | 32.8 | 59 | | 40.05 | 46.72 | 88.48 | 75.45 | 47.92 | 0.519 | 0.605 | 1.146 | 0.977 | 0.621 |
| 1.300 | 33.3 | 60 | | 40.71 | 47.49 | 89.94 | 76.70 | 48.71 | 0.529 | 0.617 | 1.169 | 0.997 | 0.633 |
| 1.305 | 33.7 | 61 | | 41.37 | 48.26 | 91.40 | 77.94 | 49.50 | 0.540 | 0.630 | 1.193 | 1.017 | 0.646 |
| 1.310 | 34.2 | 62 | | 42.06 | 49.07 | 92.94 | 79.25 | 50.33 | 0.551 | 0.643 | 1.218 | 1.038 | 0.659 |
| 1.315 | 34.6 | 63 | | 42.76 | 49.89 | 94.49 | 80.57 | 51.17 | 0.562 | 0.656 | 1.243 | 1.059 | 0.671 |
| 1.320 | 35.0 | 64 | | 43.47 | 50.71 | 96.05 | 81.90 | 52.01 | 0.573 | 0.669 | 1.268 | 1.080 | 0.686 |
| 1.325 | 35.4 | 65 | | 44.17 | 51.53 | 97.60 | 83.22 | 52.85 | 0.585 | 0.683 | 1.294 | 1.103 | 0.701 |
| 1.330 | 35.8 | 66 | | 44.89 | 52.37 | 99.19 | 84.58 | 53.71 | 0.597 | 0.697 | 1.320 | 1.126 | 0.718 |
| 1.335 | 36.2 | 67 | | 45.62 | 53.22 | 100.80 | 85.95 | 54.58 | 0.609 | 0.710 | 1.346 | 1.148 | 0.732 |
| 1.340 | 36.6 | 68 | | 46.35 | 54.07 | 102.41 | 87.32 | 55.46 | 0.621 | 0.725 | 1.373 | 1.171 | 0.744 |
| 1.345 | 37.0 | 69 | | 47.08 | 54.93 | 104.04 | 88.71 | 56.34 | 0.633 | 0.739 | 1.400 | 1.193 | 0.758 |

TABLE XCVII. (Concluded)

| Sp. Gr. 15°/4° | C. Air- free | Degrees Baumé | Degrees Fahrenheit | 100 Parts by Weight Contains | | | | | 1 Liter Contains Kilograms | | | | |
|-------------------|--------------------|------------------|-----------------------|-------------------------------|------------------|--------------------|--------------------|--------------------|-------------------------------|------------------|--------------------|--------------------|--------------------|
| | | | | N ₂ O ₄ | HNO ₃ | Acid of 36° Bé. | Acid of 40° Bé. | Acid of 48° Bé. | N ₂ O ₄ | HNO ₃ | Acid of 36° Bé. | Acid of 40° Bé. | Acid of 48° Bé. |
| 1.350 | 37.4 | 70 | 47.82 | 55.79 | 105.67 | 90.10 | 57.22 | | 0.645 | 0.753 | 1.427 | 1.216 | 0.645 |
| 1.355 | 37.6 | 71 | 48.57 | 56.66 | 107.31 | 91.51 | 58.11 | | 0.658 | 0.768 | 1.455 | 1.240 | 0.658 |
| 1.360 | 38.2 | 72 | 49.35 | 57.57 | 109.03 | 92.97 | 59.05 | | 0.671 | 0.783 | 1.483 | 1.265 | 0.671 |
| 1.365 | 38.6 | 73 | 50.13 | 58.48 | 110.75 | 94.44 | 59.98 | | 0.684 | 0.798 | 1.513 | 1.289 | 0.684 |
| 1.370 | 39.0 | 74 | 50.91 | 59.39 | 112.48 | 95.91 | 60.91 | | 0.698 | 0.814 | 1.543 | 1.314 | 0.698 |
| 1.375 | 39.4 | 75 | 51.69 | 60.30 | 114.20 | 97.38 | 61.85 | | 0.711 | 0.829 | 1.573 | 1.339 | 0.711 |
| 1.380 | 39.8 | 76 | 52.52 | 61.27 | 116.04 | 98.95 | 62.84 | | 0.725 | 0.846 | 1.603 | 1.366 | 0.725 |
| 1.3833 | 40.0 | | 53.08 | 61.92 | 117.27 | 100.00 | 63.51 | | 0.735 | 0.857 | 1.623 | 1.383 | 0.735 |
| 1.385 | 40.1 | 77 | 53.35 | 62.24 | 117.88 | 100.51 | 63.84 | | 0.739 | 0.862 | 1.633 | 1.392 | 0.739 |
| 1.390 | 40.5 | 78 | 54.20 | 63.23 | 119.75 | 102.12 | 64.85 | | 0.753 | 0.879 | 1.665 | 1.420 | 0.753 |
| 1.395 | 40.8 | 79 | 55.07 | 64.25 | 121.68 | 103.76 | 65.90 | | 0.768 | 0.896 | 1.697 | 1.447 | 0.768 |
| 1.400 | 41.2 | 80 | 55.97 | 65.30 | 123.67 | 105.46 | 66.97 | | 0.783 | 0.914 | 1.731 | 1.476 | 0.783 |
| 1.405 | 41.6 | 81 | 56.92 | 66.40 | 125.75 | 107.24 | 68.10 | | 0.800 | 0.933 | 1.767 | 1.507 | 0.800 |
| 1.410 | 42.0 | 82 | 57.86 | 67.50 | 127.84 | 109.01 | 69.23 | | 0.816 | 0.952 | 1.803 | 1.537 | 0.816 |
| 1.415 | 42.3 | 83 | 58.83 | 68.63 | 129.98 | 110.84 | 70.39 | | 0.832 | 0.971 | 1.839 | 1.568 | 0.832 |
| 1.420 | 42.7 | 84 | 59.83 | 69.80 | 132.19 | 112.73 | 71.59 | | 0.849 | 0.991 | 1.877 | 1.600 | 0.849 |
| 1.425 | 43.1 | 85 | 60.84 | 70.98 | 134.43 | 114.63 | 72.80 | | 0.867 | 1.011 | 1.915 | 1.633 | 0.867 |
| 1.430 | 43.4 | 86 | 61.80 | 72.17 | 136.68 | 116.55 | 74.02 | | 0.885 | 1.032 | 1.955 | 1.667 | 0.885 |
| 1.435 | 43.8 | 87 | 62.91 | 73.39 | 138.99 | 118.52 | 75.27 | | 0.903 | 1.053 | 1.995 | 1.701 | 0.903 |
| 1.440 | 44.1 | 88 | 64.01 | 74.68 | 141.44 | 120.61 | 76.59 | | 0.921 | 1.075 | 2.037 | 1.736 | 0.921 |
| 1.445 | 44.4 | 89 | 65.13 | 75.98 | 143.90 | 122.71 | 77.93 | | 0.941 | 1.098 | 2.080 | 1.773 | 0.941 |
| 1.450 | 44.8 | 90 | 66.24 | 77.28 | 146.36 | 124.81 | 79.26 | | 0.961 | 1.121 | 2.123 | 1.810 | 0.961 |
| 1.455 | 45.1 | 91 | 67.38 | 78.60 | 148.86 | 126.94 | 80.62 | | 0.981 | 1.144 | 2.167 | 1.848 | 0.981 |
| 1.460 | 45.4 | 92 | 68.56 | 79.98 | 151.47 | 129.17 | 82.03 | | 1.001 | 1.168 | 2.212 | 1.886 | 1.001 |
| 1.465 | 45.8 | 93 | 69.79 | 81.42 | 154.20 | 131.49 | 83.51 | | 1.023 | 1.193 | 2.259 | 1.927 | 1.023 |
| 1.470 | 46.1 | 94 | 71.06 | 82.90 | 157.00 | 133.88 | 85.03 | | 1.045 | 1.219 | 2.309 | 1.969 | 1.045 |
| 1.475 | 46.4 | 95 | 72.39 | 84.45 | 159.94 | 136.39 | 86.62 | | 1.068 | 1.246 | 2.360 | 2.012 | 1.068 |
| 1.480 | 46.8 | 96 | 73.76 | 86.05 | 162.97 | 138.97 | 88.26 | | 1.092 | 1.274 | 2.413 | 2.058 | 1.092 |
| 1.485 | 47.1 | 97 | 75.18 | 87.70 | 166.09 | 141.63 | 89.95 | | 1.116 | 1.302 | 2.466 | 2.103 | 1.116 |
| 1.490 | 47.4 | 98 | 76.80 | 89.60 | 169.69 | 144.70 | 91.90 | | 1.144 | 1.335 | 2.528 | 2.156 | 1.144 |
| 1.495 | 47.8 | 99 | 78.52 | 91.60 | 173.48 | 147.93 | 93.95 | | 1.174 | 1.369 | 2.593 | 2.211 | 1.174 |
| 1.500 | 48.1 | 100 | 80.65 | 94.09 | 178.19 | 151.96 | 96.50 | | 1.210 | 1.411 | 2.672 | 2.278 | 1.210 |
| 1.501 | | | 81.09 | 94.60 | 179.16 | 152.78 | 97.03 | | 1.217 | 1.420 | 2.689 | 2.293 | 1.217 |
| 1.502 | | | 81.50 | 95.08 | 180.07 | 153.55 | 97.52 | | 1.224 | 1.428 | 2.704 | 2.306 | 1.224 |
| 1.503 | | | 81.91 | 95.55 | 180.96 | 154.31 | 98.00 | | 1.231 | 1.436 | 2.720 | 2.319 | 1.231 |
| 1.504 | | | 82.29 | 96.00 | 181.81 | 155.04 | 98.46 | | 1.238 | 1.444 | 2.735 | 2.332 | 1.238 |
| 1.505 | 48.4 | 101 | 82.63 | 96.39 | 182.55 | 155.67 | 98.86 | | 1.244 | 1.451 | 2.748 | 2.343 | 1.244 |
| 1.506 | | | 82.94 | 96.76 | 183.25 | 156.27 | 99.27 | | 1.249 | 1.457 | 2.759 | 2.353 | 1.249 |
| 1.507 | | | 83.26 | 97.13 | 183.95 | 156.86 | 99.62 | | 1.255 | 1.464 | 2.773 | 2.364 | 1.255 |
| 1.508 | 48.5 | | 83.58 | 97.50 | 184.65 | 157.47 | 100.00 | | 1.260 | 1.470 | 2.784 | 2.374 | 1.260 |
| 1.509 | | | 83.87 | 97.84 | 185.30 | 158.01 | 100.35 | | 1.265 | 1.476 | 2.795 | 2.384 | 1.265 |
| 1.510 | 48.7 | 102 | 84.09 | 98.10 | 185.79 | 158.43 | 100.61 | | 1.270 | 1.481 | 2.805 | 2.392 | 1.270 |
| 1.511 | | | 84.28 | 98.32 | 186.21 | 158.79 | 100.84 | | 1.274 | 1.486 | 2.814 | 2.400 | 1.274 |
| 1.512 | | | 84.46 | 98.53 | 186.61 | 159.13 | 101.06 | | 1.277 | 1.490 | 2.822 | 2.406 | 1.277 |
| 1.513 | | | 84.63 | 98.73 | 186.98 | 159.45 | 101.26 | | 1.280 | 1.494 | 2.829 | 2.413 | 1.280 |
| 1.514 | | | 84.78 | 98.90 | 187.30 | 159.72 | 101.44 | | 1.283 | 1.497 | 2.835 | 2.418 | 1.283 |
| 1.515 | 49.0 | 103 | 84.92 | 99.07 | 187.63 | 160.00 | 101.61 | | 1.287 | 1.501 | 2.843 | 2.424 | 1.287 |
| 1.516 | | | 85.04 | 99.21 | 187.89 | 160.22 | 101.75 | | 1.289 | 1.504 | 2.848 | 2.429 | 1.289 |
| 1.517 | | | 85.15 | 99.34 | 188.14 | 160.43 | 101.89 | | 1.292 | 1.507 | 2.854 | 2.434 | 1.292 |
| 1.518 | | | 85.26 | 99.46 | 188.37 | 160.63 | 102.01 | | 1.294 | 1.510 | 2.860 | 2.439 | 1.294 |
| 1.519 | | | 85.35 | 99.57 | 188.58 | 160.81 | 102.12 | | 1.296 | 1.512 | 2.864 | 2.442 | 1.296 |
| 1.520 | 49.4 | 104 | 85.44 | 99.67 | 188.77 | 160.97 | 102.23 | | 1.299 | 1.515 | 2.869 | 2.447 | 1.299 |

TABLE XCVIII.—CORRECTION OF SPECIFIC GRAVITY OF NITRIC ACID CONTAINING NITROUS FUMES (LUNGE AND MARCHLEWSKI)

The correction given is to be subtracted from the Sp. Gr. of nitric acid at 15° C. (1.49 compared to water at 4° C. = 1) to give the Sp. Gr. corresponding to the nitric acid actually present.

| N ₂ O ₄ % | Correction | N ₂ O ₄ % | Correction | N ₂ O ₄ % | Correction | N ₂ O ₄ % | Correction |
|------------------------------------|------------|------------------------------------|------------|------------------------------------|------------|------------------------------------|------------|
| 0.25 | 0.0005 | 3.50 | 0.0217 | 6.75 | 0.0448 | 10.00 | 0.0680 |
| 0.50 | 0.0008 | 3.75 | 0.0235 | 7.00 | 0.0465 | 10.25 | 0.0682 |
| 0.75 | 0.0015 | 4.00 | 0.0253 | 7.25 | 0.0472 | 10.50 | 0.0698 |
| 1.00 | 0.0030 | 4.25 | 0.0269 | 7.50 | 0.0500 | 10.75 | 0.0714 |
| 1.25 | 0.0048 | 4.50 | 0.0288 | 7.75 | 0.0517 | 11.00 | 0.0730 |
| 1.50 | 0.0068 | 4.75 | 0.0305 | 8.00 | 0.0533 | 11.25 | 0.0746 |
| 1.75 | 0.0078 | 5.00 | 0.0323 | 8.25 | 0.0550 | 11.50 | 0.0760 |
| 2.00 | 0.0105 | 5.25 | 0.0337 | 8.50 | 0.0566 | 11.75 | 0.0775 |
| 2.25 | 0.0125 | 5.50 | 0.0360 | 8.75 | 0.0583 | 12.00 | 0.0785 |
| 2.50 | 0.0143 | 5.75 | 0.0378 | 9.00 | 0.0600 | 12.25 | 0.0805 |
| 2.75 | 0.0163 | 6.00 | 0.0395 | 9.25 | 0.0616 | 12.50 | 0.0820 |
| 3.00 | 0.0180 | 6.25 | 0.0418 | 9.50 | 0.0633 | 12.75 | 0.0835 |
| 3.25 | 0.0199 | 6.50 | 0.0430 | 9.75 | 0.0650 | | |

TABLE XCIX.—DENSITIES OF CONCENTRATED NITRIC ACID AT DIFFERENT TEMPERATURES

(From V. H. VELEY AND J. J. MANLEY, J. S. C. I. 1903, 22, 1227)

| At 4° | 10°/4° | Densities 15°/4° | 20°/4° | 25°/4° | Per- centages |
|--------|--------|---------------------|--------|--------|------------------|
| 1.400 | 1.392 | 1.385 | 1.378 | 1.371 | 62.3 |
| 1.401 | 1.393 | 1.386 | 1.379 | 1.372 | 62.5 |
| 1.402 | 1.394 | 1.387 | 1.380 | 1.373 | 62.7 |
| 1.403 | 1.395 | 1.388 | 1.381 | 1.374 | 62.9 |
| 1.404 | 1.396 | 1.3895 | 1.382 | 1.375 | 63.1 |
| 1.405 | 1.397 | 1.391 | 1.383 | 1.376 | 63.3 |
| 1.406 | 1.398 | 1.392 | 1.384 | 1.377 | 63.5 |
| 1.407 | 1.399 | 1.393 | 1.385 | 1.378 | 63.7 |
| 1.408 | 1.400 | 1.394 | 1.386 | 1.379 | 63.9 |
| 1.409 | 1.401 | 1.395 | 1.387 | 1.380 | 64.1 |
| 1.410 | 1.402 | 1.396 | 1.388 | 1.381 | 64.3 |
| 1.411 | 1.403 | 1.397 | 1.389 | 1.382 | 64.5 |
| 1.412 | 1.404 | 1.398 | 1.390 | 1.382 | 64.7 |
| 1.413 | 1.405 | 1.399 | 1.391 | 1.383 | 64.9 |
| 1.414 | 1.406 | 1.3995 | 1.392 | 1.384 | 65.1 |
| 1.415 | 1.407 | 1.400 | 1.393 | 1.385 | 65.3 |
| 1.416 | 1.408 | 1.401 | 1.394 | 1.386 | 65.4 |
| 1.417 | 1.409 | 1.402 | 1.394 | 1.386 | 65.6 |
| 1.418 | 1.410 | 1.403 | 1.395 | 1.387 | 65.8 |
| 1.419 | 1.411 | 1.404 | 1.396 | 1.388 | 66.0 |
| 1.420 | 1.412 | 1.405 | 1.397 | 1.389 | 66.2 |
| 1.421 | 1.413 | 1.406 | 1.398 | 1.390 | 66.4 |
| 1.422 | 1.414 | 1.4065 | 1.399 | 1.391 | 66.6 |
| 1.423 | 1.415 | 1.407 | 1.400 | 1.392 | 66.8 |
| 1.424 | 1.416 | 1.408 | 1.401 | 1.393 | 67.0 |
| 1.425 | 1.417 | 1.409 | 1.402 | 1.394 | 67.2 |
| 1.426 | 1.418 | 1.410 | 1.402 | 1.394 | 67.4 |
| 1.427 | 1.419 | 1.411 | 1.403 | 1.395 | 67.6 |
| 1.428 | 1.420 | 1.412 | 1.404 | 1.396 | 67.8 |
| 1.429 | 1.421 | 1.4125 | 1.405 | 1.397 | 68.0 |
| 1.430 | 1.422 | 1.413 | 1.406 | 1.398 | 68.2 |
| 1.431 | 1.423 | 1.414 | 1.407 | 1.398 | 68.4 |
| 1.432 | 1.423 | 1.415 | 1.408 | 1.399 | 68.6 |
| 1.433 | 1.424 | 1.416 | 1.408 | 1.400 | 68.8 |
| 1.434 | 1.425 | 1.417 | 1.409 | 1.401 | 69.0 |
| 1.435 | 1.426 | 1.418 | 1.410 | 1.402 | 69.2 |
| 1.436 | 1.427 | 1.419 | 1.411 | 1.403 | 69.4 |
| 1.437 | 1.428 | 1.420 | 1.412 | 1.404 | 69.6 |
| 1.438 | 1.429 | 1.4205 | 1.413 | 1.405 | 69.8 |
| 1.439 | 1.4295 | 1.421 | 1.414 | 1.406 | 70.0 |
| 1.440 | 1.430 | 1.422 | 1.415 | 1.407 | 70.2 |
| 1.441 | 1.431 | 1.423 | 1.416 | 1.408 | 70.4 |
| 1.442 | 1.432 | 1.424 | 1.417 | 1.409 | 70.6 |
| 1.443 | 1.433 | 1.425 | 1.418 | 1.410 | 70.8 |
| 1.444 | 1.434 | 1.426 | 1.419 | 1.411 | 71.0 |
| 1.445 | 1.435 | 1.427 | 1.420 | 1.412 | 71.2 |
| 1.446 | 1.436 | 1.428 | 1.421 | 1.413 | 71.4 |
| 1.447 | 1.437 | 1.429 | 1.422 | 1.414 | 71.7 |
| 1.448 | 1.438 | 1.430 | 1.423 | 1.415 | 72.0 |
| 1.449 | 1.439 | 1.431 | 1.424 | 1.416 | 72.3 |
| 1.450 | 1.440 | 1.432 | 1.425 | 1.417 | 72.5 |
| 1.451 | 1.441 | 1.433 | 1.426 | 1.418 | 72.7 |
| 1.452 | 1.442 | 1.434 | 1.427 | 1.419 | 73.0 |
| 1.453 | 1.443 | 1.435 | 1.428 | 1.420 | 73.3 |
| 1.454 | 1.444 | 1.436 | 1.429 | 1.421 | 73.5 |
| 1.455 | 1.445 | 1.437 | 1.430 | 1.422 | 73.7 |
| 1.456 | 1.446 | 1.438 | 1.431 | 1.423 | 74.0 |
| 1.457 | 1.447 | 1.439 | 1.432 | 1.424 | 74.2 |
| 1.458 | 1.448 | 1.440 | 1.433 | 1.425 | 74.5 |
| 1.459 | 1.449 | 1.441 | 1.434 | 1.426 | 74.7 |
| 1.460 | 1.450 | 1.442 | 1.435 | 1.427 | 74.9 |
| 1.461 | 1.451 | 1.443 | 1.436 | 1.428 | 75.2 |
| 1.462 | 1.452 | 1.444 | 1.437 | 1.429 | 75.5 |
| 1.463 | 1.453 | 1.445 | 1.438 | 1.430 | 75.7 |
| 1.464 | 1.454 | 1.446 | 1.439 | 1.431 | 75.9 |
| 1.465 | 1.455 | 1.447 | 1.440 | 1.432 | 76.2 |
| 1.466 | 1.456 | 1.448 | 1.441 | 1.433 | 76.5 |
| 1.467 | 1.457 | 1.449 | 1.442 | 1.434 | 76.8 |
| 1.468 | 1.458 | 1.450 | 1.4425 | 1.435 | 77.0 |
| 1.469 | 1.459 | 1.451 | 1.443 | 1.436 | 77.3 |
| 1.470 | 1.460 | 1.452 | 1.444 | 1.437 | 77.6 |
| 1.471 | 1.461 | 1.453 | 1.445 | 1.438 | 77.9 |
| 1.472 | 1.462 | 1.454 | 1.446 | 1.439 | 78.2 |
| 1.4725 | 1.4625 | 1.4545 | 1.4465 | 1.4395 | 78.5 |
| 1.473 | 1.463 | 1.455 | 1.447 | 1.440 | 78.8 |

TABLE XCIX. (Concluded)

| At 4° | 10°/4° | Densities 15°/4° | 20°/4° | 25°/4° | Per- centages |
|--------|--------|---------------------|--------|--------|------------------|
| 1.474 | 1.464 | 1.456 | 1.448 | 1.441 | 79.1 |
| 1.475 | 1.465 | 1.457 | 1.449 | 1.442 | 79.4 |
| 1.476 | 1.466 | 1.458 | 1.450 | 1.443 | 79.7 |
| 1.477 | 1.667 | 1.459 | 1.451 | 1.444 | 80.0 |
| 1.478 | 1.468 | 1.460 | 1.452 | 1.445 | 80.3 |
| 1.479 | 1.469 | 1.461 | 1.453 | 1.446 | 80.6 |
| 1.480 | 1.470 | 1.462 | 1.454 | 1.4465 | 80.9 |
| 1.481 | 1.471 | 1.463 | 1.455 | 1.447 | 81.2 |
| 1.482 | 1.472 | 1.464 | 1.456 | 1.448 | 81.5 |
| 1.483 | 1.473 | 1.465 | 1.457 | 1.449 | 81.8 |
| 1.484 | 1.474 | 1.466 | 1.458 | 1.450 | 82.1 |
| 1.485 | 1.475 | 1.467 | 1.459 | 1.451 | 82.4 |
| 1.487 | 1.476 | 1.468 | 1.460 | 1.452 | 82.7 |
| 1.488 | 1.477 | 1.469 | 1.461 | 1.453 | 83.0 |
| 1.489 | 1.478 | 1.470 | 1.462 | 1.454 | 83.3 |
| 1.490 | 1.479 | 1.471 | 1.463 | 1.455 | 83.6 |
| 1.491 | 1.480 | 1.472 | 1.464 | 1.456 | 83.9 |
| 1.492 | 1.481 | 1.473 | 1.465 | 1.457 | 84.2 |
| 1.493 | 1.482 | 1.474 | 1.466 | 1.4575 | 84.5 |
| 1.494 | 1.483 | 1.475 | 1.467 | 1.458 | 84.8 |
| 1.495 | 1.484 | 1.476 | 1.468 | 1.459 | 85.1 |
| 1.496 | 1.486 | 1.477 | 1.469 | 1.460 | 85.4 |
| 1.497 | 1.487 | 1.478 | 1.470 | 1.461 | 85.7 |
| 1.498 | 1.488 | 1.479 | 1.471 | 1.462 | 86.0 |
| 1.499 | 1.489 | 1.480 | 1.472 | 1.463 | 86.3 |
| 1.500 | 1.490 | 1.481 | 1.473 | 1.464 | 86.6 |
| 1.501 | 1.491 | 1.482 | 1.4735 | 1.465 | 86.9 |
| 1.502 | 1.492 | 1.483 | 1.474 | 1.466 | 87.2 |
| 1.503 | 1.4925 | 1.4845 | 1.475 | 1.4665 | 87.5 |
| 1.504 | 1.493 | 1.485 | 1.476 | 1.467 | 87.8 |
| 1.505 | 1.494 | 1.485 | 1.477 | 1.468 | 88.1 |
| 1.506 | 1.495 | 1.486 | 1.478 | 1.469 | 88.4 |
| 1.507 | 1.496 | 1.487 | 1.479 | 1.470 | 88.7 |
| 1.508 | 1.497 | 1.488 | 1.480 | 1.471 | 89.0 |
| 1.509 | 1.498 | 1.489 | 1.481 | 1.472 | 89.3 |
| 1.510 | 1.499 | 1.490 | 1.482 | 1.473 | 89.6 |
| 1.511 | 1.500 | 1.491 | 1.4825 | 1.474 | 89.9 |
| 1.512 | 1.501 | 1.492 | 1.483 | 1.475 | 90.2 |
| 1.513 | 1.502 | 1.493 | 1.484 | 1.476 | 90.5 |
| 1.514 | 1.503 | 1.494 | 1.485 | 1.477 | 90.8 |
| 1.515 | 1.504 | 1.495 | 1.486 | 1.4775 | 91.1 |
| 1.516 | 1.505 | 1.496 | 1.487 | 1.478 | 91.4 |
| 1.517 | 1.506 | 1.497 | 1.488 | 1.479 | 91.7 |
| 1.518 | 1.507 | 1.498 | 1.489 | 1.480 | 92.0 |
| 1.519 | 1.508 | 1.499 | 1.490 | 1.481 | 92.3 |
| 1.5195 | 1.5085 | 1.4995 | 1.4905 | 1.482 | 92.6 |
| 1.520 | 1.509 | 1.500 | 1.491 | 1.483 | 93.0 |
| 1.520 | 1.509 | 1.500 | 1.492 | 1.484 | 93.5 |
| 1.520 | 1.509 | 1.500 | 1.492 | 1.485 | 94.0 |
| 1.521 | 1.510 | 1.501 | 1.493 | 1.485 | 94.5 |
| 1.522 | 1.511 | 1.502 | 1.494 | 1.486 | 95.0 |
| 1.523 | 1.512 | 1.503 | 1.495 | 1.487 | 95.5 |
| 1.524 | 1.513 | 1.504 | 1.496 | 1.488 | 96.0 |
| 1.525 | 1.514 | 1.505 | 1.497 | 1.489 | 96.5 |
| 1.527 | 1.516 | 1.507 | 1.498 | 1.490 | 97.0 |
| 1.528 | 1.517 | 1.508 | 1.499 | 1.491 | 97.2 |
| 1.529 | 1.518 | 1.509 | 1.500 | 1.492 | 97.5 |
| 1.530 | 1.519 | 1.510 | 1.501 | 1.4925 | 97.8 |
| 1.531 | 1.520 | 1.511 | 1.502 | 1.493 | 98.0 |
| 1.532 | 1.521 | 1.512 | 1.503 | 1.494 | 98.3 |
| 1.533 | 1.522 | 1.513 | 1.504 | 1.495 | 98.6 |
| 1.535 | 1.524 | 1.516 | 1.506 | 1.496 | 98.9 |
| 1.537 | 1.526 | 1.517 | 1.507 | 1.497 | 99.2 |
| 1.538 | 1.527 | 1.518 | 1.508 | 1.498 | 99.5 |
| 1.540 | 1.529 | 1.520 | 1.509 | 1.4985 | 99.8 |
| 1.542 | 1.530 | 1.521 | 1.510 | 1.499 | 100.0 |

If results at 30° C. are desired, the figures in Table XCIX could be used after making corrections as follows:

| Values to be Subtracted from Values at 25°/4° C. | Percentages |
|---|-------------|
| 0.007 | 85—85 |
| 0.008 | 85—85 |
| 0.009 | 85—93 |
| 0.008 | 93—98 |
| 0.010 | 98—100 |

It has been observed that acid of 90% and greater concentrations could not be heated above 25° C. without the formation of nitrogen peroxide.

TABLE C.—NITRIC ACID

By W. C. Farnouson

| Degrees Baumé | Specific Gravity 60°/60° F. | Degrees Twaddell | Per cent. HNO ₃ | Degrees Baumé | Specific Gravity 60°/60° F. | Degrees Twaddell | Per cent. HNO ₃ |
|------------------|-----------------------------------|---------------------|-------------------------------|------------------|-----------------------------------|---------------------|-------------------------------|
| 10.00 | 1.0741 | 14.82 | 12.86 | 27.00 | 1.2288 | 45.76 | 36.48 |
| 10.25 | 1.0761 | 15.22 | 13.18 | 27.25 | 1.2314 | 46.28 | 36.87 |
| 10.50 | 1.0781 | 15.62 | 13.49 | 27.50 | 1.2340 | 46.80 | 37.26 |
| 10.75 | 1.0801 | 16.02 | 13.81 | 27.75 | 1.2367 | 47.34 | 37.67 |
| 11.00 | 1.0821 | 16.42 | 14.13 | 28.00 | 1.2393 | 47.86 | 38.06 |
| 11.25 | 1.0841 | 16.82 | 14.44 | 28.25 | 1.2420 | 48.40 | 38.46 |
| 11.50 | 1.0861 | 17.22 | 14.76 | 28.50 | 1.2446 | 48.92 | 38.85 |
| 11.75 | 1.0881 | 17.62 | 15.07 | 28.75 | 1.2473 | 49.46 | 39.25 |
| 12.00 | 1.0902 | 18.04 | 15.41 | 29.00 | 1.2500 | 50.00 | 39.66 |
| 12.25 | 1.0922 | 18.44 | 15.72 | 29.25 | 1.2527 | 50.54 | 40.06 |
| 12.50 | 1.0943 | 18.86 | 16.05 | 29.50 | 1.2554 | 51.08 | 40.47 |
| 12.75 | 1.0964 | 19.28 | 16.39 | 29.75 | 1.2582 | 51.64 | 40.89 |
| 13.00 | 1.0985 | 19.70 | 16.72 | 30.00 | 1.2609 | 52.18 | 41.30 |
| 13.25 | 1.1006 | 20.12 | 17.05 | 30.25 | 1.2637 | 52.74 | 41.72 |
| 13.50 | 1.1027 | 20.54 | 17.38 | 30.50 | 1.2664 | 53.28 | 42.14 |
| 13.75 | 1.1048 | 20.96 | 17.71 | 30.75 | 1.2692 | 53.84 | 42.58 |
| 14.00 | 1.1069 | 21.38 | 18.04 | 31.00 | 1.2719 | 54.38 | 43.00 |
| 14.25 | 1.1090 | 21.80 | 18.37 | 31.25 | 1.2747 | 54.94 | 43.44 |
| 14.50 | 1.1111 | 22.22 | 18.70 | 31.50 | 1.2775 | 55.50 | 43.89 |
| 14.75 | 1.1132 | 22.64 | 19.02 | 31.75 | 1.2804 | 56.08 | 44.34 |
| 15.00 | 1.1154 | 23.08 | 19.36 | 32.00 | 1.2832 | 56.64 | 44.78 |
| 15.25 | 1.1176 | 23.52 | 19.70 | 32.25 | 1.2861 | 57.22 | 45.24 |
| 15.50 | 1.1197 | 23.94 | 20.02 | 32.50 | 1.2889 | 57.78 | 45.68 |
| 15.75 | 1.1219 | 24.38 | 20.36 | 32.75 | 1.2918 | 58.36 | 46.14 |
| 16.00 | 1.1240 | 24.80 | 20.69 | 33.00 | 1.2946 | 58.92 | 46.58 |
| 16.25 | 1.1262 | 25.24 | 21.03 | 33.25 | 1.2975 | 59.50 | 47.04 |
| 16.50 | 1.1284 | 25.68 | 21.36 | 33.50 | 1.3004 | 60.08 | 47.49 |
| 16.75 | 1.1306 | 26.12 | 21.70 | 33.75 | 1.3034 | 60.68 | 47.95 |
| 17.00 | 1.1328 | 26.56 | 22.04 | 34.00 | 1.3063 | 61.26 | 48.42 |
| 17.25 | 1.1350 | 27.00 | 22.38 | 34.25 | 1.3093 | 61.86 | 48.90 |
| 17.50 | 1.1373 | 27.46 | 22.74 | 34.50 | 1.3122 | 62.44 | 49.35 |
| 17.75 | 1.1395 | 27.90 | 23.08 | 34.75 | 1.3152 | 63.04 | 49.83 |
| 18.00 | 1.1417 | 28.34 | 23.42 | 35.00 | 1.3182 | 63.64 | 50.32 |
| 18.25 | 1.1440 | 28.80 | 23.77 | 35.25 | 1.3212 | 64.24 | 50.81 |
| 18.50 | 1.1462 | 29.24 | 24.11 | 35.50 | 1.3242 | 64.84 | 51.30 |
| 18.75 | 1.1485 | 29.70 | 24.47 | 35.75 | 1.3273 | 65.46 | 51.80 |
| 19.00 | 1.1508 | 30.16 | 24.82 | 36.00 | 1.3303 | 66.06 | 52.30 |
| 19.25 | 1.1531 | 30.62 | 25.18 | 36.25 | 1.3334 | 66.68 | 52.81 |
| 19.50 | 1.1554 | 31.08 | 25.53 | 36.50 | 1.3364 | 67.28 | 53.32 |
| 19.75 | 1.1577 | 31.54 | 25.88 | 36.75 | 1.3395 | 67.90 | 53.84 |
| 20.00 | 1.1600 | 32.00 | 26.24 | 37.00 | 1.3426 | 68.52 | 54.36 |
| 20.25 | 1.1624 | 32.48 | 26.61 | 37.25 | 1.3457 | 69.14 | 54.89 |
| 20.50 | 1.1647 | 32.94 | 26.96 | 37.50 | 1.3488 | 69.76 | 55.43 |
| 20.75 | 1.1671 | 33.42 | 27.33 | 37.75 | 1.3520 | 70.40 | 55.97 |
| 21.00 | 1.1694 | 33.88 | 27.67 | 38.00 | 1.3551 | 71.02 | 56.52 |
| 21.25 | 1.1718 | 34.36 | 28.02 | 38.25 | 1.3583 | 71.66 | 57.08 |
| 21.50 | 1.1741 | 34.82 | 28.36 | 38.50 | 1.3615 | 72.30 | 57.65 |
| 21.75 | 1.1765 | 35.30 | 28.72 | 38.75 | 1.3647 | 72.94 | 58.23 |
| 22.00 | 1.1789 | 35.78 | 29.07 | 39.00 | 1.3679 | 73.58 | 58.82 |
| 22.25 | 1.1813 | 36.26 | 29.43 | 39.25 | 1.3712 | 74.24 | 59.43 |
| 22.50 | 1.1837 | 36.74 | 29.78 | 39.50 | 1.3744 | 74.88 | 60.06 |
| 22.75 | 1.1861 | 37.22 | 30.14 | 39.75 | 1.3777 | 75.54 | 60.71 |
| 23.00 | 1.1885 | 37.70 | 30.49 | 40.00 | 1.3810 | 76.20 | 61.38 |
| 23.25 | 1.1910 | 38.20 | 30.86 | 40.25 | 1.3843 | 76.86 | 62.07 |
| 23.50 | 1.1934 | 38.68 | 31.21 | 40.50 | 1.3876 | 77.52 | 62.77 |
| 23.75 | 1.1959 | 39.18 | 31.58 | 40.75 | 1.3909 | 78.18 | 63.45 |
| 24.00 | 1.1983 | 39.66 | 31.94 | 41.00 | 1.3942 | 78.84 | 64.20 |
| 24.25 | 1.2008 | 40.16 | 32.31 | 41.25 | 1.3976 | 79.52 | 64.93 |
| 24.50 | 1.2033 | 40.66 | 32.68 | 41.50 | 1.4010 | 80.20 | 65.67 |
| 24.75 | 1.2058 | 41.16 | 33.05 | 41.75 | 1.4044 | 80.88 | 66.42 |
| 25.00 | 1.2083 | 41.66 | 33.42 | 42.00 | 1.4078 | 81.56 | 67.18 |
| 25.25 | 1.2109 | 42.18 | 33.80 | 42.25 | 1.4112 | 82.24 | 67.95 |
| 25.50 | 1.2134 | 42.68 | 34.17 | 42.50 | 1.4146 | 82.92 | 68.73 |
| 25.75 | 1.2160 | 43.20 | 34.56 | 42.75 | 1.4181 | 83.62 | 69.52 |
| 26.00 | 1.2185 | 43.70 | 34.94 | 43.00 | 1.4216 | 84.32 | 70.32 |
| 26.25 | 1.2211 | 44.22 | 35.33 | 43.25 | 1.4251 | 85.02 | 71.15 |
| 26.50 | 1.2236 | 44.72 | 35.70 | 43.50 | 1.4286 | 85.72 | 71.98 |
| 26.75 | 1.2262 | 45.24 | 36.09 | 43.75 | 1.4321 | 86.42 | 72.82 |

TABLE C. (Concluded)

| Degrees Baumé | Specific Gravity 60°/60° F. | Degrees Twaddell | Per cent. HNO ₃ | Degrees Baumé | Specific Gravity 60°/60° F. | Degrees Twaddell | Per cent. HNO ₃ |
|------------------|-----------------------------------|---------------------|-------------------------------|------------------|-----------------------------------|---------------------|-------------------------------|
| 44.00 | 1.4356 | 87.12 | 73.67 | 46.50 | 1.4721 | 94.42 | 83.33 |
| 44.25 | 1.4392 | 87.84 | 74.53 | 46.75 | 1.4758 | 95.16 | 84.48 |
| 44.50 | 1.4428 | 88.56 | 75.40 | 47.00 | 1.4796 | 95.92 | 85.70 |
| 44.75 | 1.4464 | 89.28 | 76.28 | 47.25 | 1.4834 | 96.68 | 86.96 |
| 45.00 | 1.4500 | 90.00 | 77.17 | 47.50 | 1.4872 | 97.44 | 88.32 |
| 45.25 | 1.4536 | 90.72 | 78.07 | 47.75 | 1.4910 | 98.20 | 89.76 |
| 45.50 | 1.4573 | 91.46 | 79.03 | 48.00 | 1.4948 | 98.96 | 91.35 |
| 45.75 | 1.4610 | 92.20 | 80.04 | 48.25 | 1.4987 | 99.74 | 93.13 |
| 46.00 | 1.4646 | 92.92 | 81.08 | 48.50 | 1.5026 | 100.52 | 95.11 |
| 46.25 | 1.4684 | 93.68 | 82.18 | | | | |

Specific gravity determinations were made at 60° F., compared with water at 60° F. From the specific gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{specific gravity}}$$

Baumé hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. () = 16.

ALLOWANCE FOR TEMPERATURE

At 10°-20° Bé. $-\frac{1}{100}$ Bé. or 0.00029 specific gravity = 1° F.
 20°-30° Bé. $-\frac{1}{100}$ Bé. or 0.00044 specific gravity = 1° F.
 30°-40° Bé. $-\frac{1}{100}$ Bé. or 0.00060 specific gravity = 1° F.
 40°-48.5° Bé. $-\frac{1}{100}$ Bé. or 0.00084 specific gravity = 1° F.

AUTHORITY—W. C. FERGUSON

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
 HENRY HOWARD, ARTHUR WYMAN,
 A. G. ROSENGARTEN,

New York, May 14, 1903.

Executive Committee.

TABLE CI.—WEIGHT OF 1 CC. OF MOIST NITROGEN IN MILLIGRAMS AT VARIOUS TEMPERATURES AND PRESSURES*

| Temperature, ° C. | 726 | 728 | 730 | 732 | 734 | 736 | 738 | 740 | 742 | 744 | 746 | 748 | 750 |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 15..... | 1.114 | 1.117 | 1.120 | 1.123 | 1.127 | 1.130 | 1.133 | 1.136 | 1.139 | 1.142 | 1.145 | 1.148 | 1.151 |
| 16..... | 1.109 | 1.112 | 1.115 | 1.118 | 1.121 | 1.125 | 1.128 | 1.131 | 1.134 | 1.137 | 1.140 | 1.143 | 1.146 |
| 17..... | 1.104 | 1.107 | 1.110 | 1.113 | 1.116 | 1.120 | 1.123 | 1.126 | 1.129 | 1.132 | 1.135 | 1.138 | 1.141 |
| 18..... | 1.098 | 1.101 | 1.105 | 1.108 | 1.111 | 1.114 | 1.117 | 1.120 | 1.123 | 1.126 | 1.129 | 1.133 | 1.136 |
| 19..... | 1.093 | 1.096 | 1.099 | 1.102 | 1.106 | 1.109 | 1.112 | 1.115 | 1.118 | 1.121 | 1.124 | 1.127 | 1.130 |
| 20..... | 1.088 | 1.091 | 1.094 | 1.097 | 1.100 | 1.103 | 1.106 | 1.109 | 1.112 | 1.116 | 1.119 | 1.122 | 1.125 |
| 21..... | 1.082 | 1.085 | 1.088 | 1.092 | 1.095 | 1.098 | 1.101 | 1.104 | 1.107 | 1.110 | 1.113 | 1.116 | 1.119 |
| 22..... | 1.077 | 1.080 | 1.083 | 1.086 | 1.089 | 1.092 | 1.095 | 1.098 | 1.101 | 1.104 | 1.107 | 1.111 | 1.114 |
| 23..... | 1.071 | 1.074 | 1.077 | 1.080 | 1.084 | 1.087 | 1.090 | 1.093 | 1.096 | 1.099 | 1.102 | 1.105 | 1.108 |
| 24..... | 1.066 | 1.069 | 1.072 | 1.075 | 1.078 | 1.081 | 1.084 | 1.087 | 1.090 | 1.093 | 1.096 | 1.099 | 1.102 |
| 25..... | 1.060 | 1.063 | 1.066 | 1.069 | 1.072 | 1.075 | 1.078 | 1.081 | 1.084 | 1.087 | 1.090 | 1.093 | 1.096 |
| 26..... | 1.054 | 1.057 | 1.060 | 1.063 | 1.066 | 1.069 | 1.072 | 1.075 | 1.079 | 1.082 | 1.085 | 1.088 | 1.091 |
| 27..... | 1.049 | 1.052 | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 | 1.070 | 1.073 | 1.076 | 1.079 | 1.082 | 1.085 |
| 28..... | 1.043 | 1.046 | 1.049 | 1.052 | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 | 1.070 | 1.073 | 1.076 | 1.079 |
| 29..... | 1.037 | 1.040 | 1.043 | 1.046 | 1.049 | 1.052 | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 | 1.070 | 1.073 |
| 30..... | 1.031 | 1.034 | 1.037 | 1.040 | 1.043 | 1.046 | 1.049 | 1.052 | 1.055 | 1.058 | 1.061 | 1.064 | 1.067 |
| 15..... | 750 | 752 | 754 | 756 | 758 | 760 | 762 | 764 | 766 | 768 | 770 | | |
| 16..... | 1.152 | 1.155 | 1.158 | 1.161 | 1.164 | 1.167 | 1.170 | 1.174 | 1.177 | 1.180 | 1.183 | | |
| 17..... | 1.146 | 1.150 | 1.153 | 1.156 | 1.159 | 1.162 | 1.165 | 1.168 | 1.171 | 1.174 | 1.178 | | |
| 18..... | 1.141 | 1.144 | 1.147 | 1.150 | 1.154 | 1.157 | 1.160 | 1.163 | 1.166 | 1.169 | 1.172 | | |
| 19..... | 1.136 | 1.139 | 1.142 | 1.145 | 1.148 | 1.151 | 1.154 | 1.157 | 1.160 | 1.164 | 1.167 | | |
| 20..... | 1.130 | 1.133 | 1.136 | 1.140 | 1.143 | 1.146 | 1.149 | 1.152 | 1.155 | 1.158 | 1.161 | | |
| 21..... | 1.125 | 1.128 | 1.131 | 1.134 | 1.137 | 1.140 | 1.143 | 1.146 | 1.149 | 1.152 | 1.156 | | |
| 22..... | 1.119 | 1.122 | 1.125 | 1.128 | 1.131 | 1.135 | 1.138 | 1.141 | 1.144 | 1.147 | 1.150 | | |
| 23..... | 1.114 | 1.117 | 1.120 | 1.123 | 1.126 | 1.129 | 1.132 | 1.135 | 1.138 | 1.141 | 1.144 | | |
| 24..... | 1.108 | 1.111 | 1.114 | 1.117 | 1.120 | 1.123 | 1.126 | 1.129 | 1.132 | 1.135 | 1.138 | | |
| 25..... | 1.102 | 1.105 | 1.108 | 1.111 | 1.114 | 1.117 | 1.120 | 1.124 | 1.127 | 1.130 | 1.133 | | |
| 26..... | 1.096 | 1.099 | 1.102 | 1.105 | 1.108 | 1.112 | 1.115 | 1.118 | 1.121 | 1.124 | 1.127 | | |
| 27..... | 1.091 | 1.094 | 1.097 | 1.100 | 1.103 | 1.106 | 1.109 | 1.112 | 1.115 | 1.118 | 1.121 | | |
| 28..... | 1.085 | 1.088 | 1.091 | 1.094 | 1.097 | 1.100 | 1.103 | 1.106 | 1.109 | 1.112 | 1.115 | | |
| 29..... | 1.079 | 1.082 | 1.085 | 1.088 | 1.091 | 1.094 | 1.097 | 1.100 | 1.103 | 1.106 | 1.109 | | |
| 30..... | 1.073 | 1.076 | 1.079 | 1.082 | 1.085 | 1.088 | 1.091 | 1.093 | 1.096 | 1.099 | 1.102 | | |
| 40..... | 1.066 | 1.069 | 1.072 | 1.075 | 1.078 | 1.081 | 1.084 | 1.087 | 1.090 | 1.093 | 1.096 | | |

* This table is based on the weight of 1 liter of nitrogen at 0° C. and 760 mm., which is 1.2514 grams. Interpolations should be made for fractions of a degree and barometric pressures intermediate between those shown.

TABLE CII.—CORRECTION FACTORS FOR REDUCING VOLUME OF NITRIC OXIDE (NO) IN CUBIC CENTIMETERS OBSERVED ON LUNGE NITROMETER TO VOLUME IN CUBIC CENTIMETERS AT 0° C. AND 760 MM. PRESSURE.

| [cc. in nitrometer × factor = number of cc. at 0° C. and 760 mm. pressure] | | | | | | | | | |
|--|-------------------|--------|--------|--------|--------|--------|--------|--------|--|
| 100 | | | | | | | | | |
| Barometric Pressure, Mm. of Mercury | Temperature, ° C. | | | | | | | | |
| | 3° | 3.2° | 3.4° | 3.6° | 3.8° | 4° | 4.2° | 4.4° | |
| 775 | 100.86 | 100.79 | 100.71 | 100.64 | 100.57 | 100.50 | 100.43 | 100.35 | |
| 774 | 100.73 | 100.66 | 100.58 | 100.51 | 100.44 | 100.37 | 100.30 | 100.22 | |
| 773 | 100.60 | 100.53 | 100.45 | 100.38 | 100.31 | 100.24 | 100.17 | 100.09 | |
| 772 | 100.47 | 100.40 | 100.32 | 100.25 | 100.18 | 100.11 | 100.04 | 99.96 | |
| 771 | 100.34 | 100.27 | 100.19 | 100.12 | 100.05 | 99.98 | 99.91 | 99.83 | |
| 770 | 100.21 | 100.14 | 100.06 | 99.99 | 99.92 | 99.85 | 99.78 | 99.70 | |
| 769 | 100.08 | 100.01 | 99.93 | 99.86 | 99.79 | 99.72 | 99.66 | 99.58 | |
| 768 | 99.95 | 99.88 | 99.80 | 99.73 | 99.66 | 99.59 | 99.53 | 99.45 | |
| 767 | 99.82 | 99.75 | 99.67 | 99.60 | 99.53 | 99.46 | 99.40 | 99.32 | |
| 766 | 99.69 | 99.62 | 99.54 | 99.47 | 99.40 | 99.33 | 99.27 | 99.19 | |
| 765 | 99.56 | 99.49 | 99.41 | 99.34 | 99.27 | 99.20 | 99.14 | 99.06 | |
| 764 | 99.43 | 99.36 | 99.28 | 99.21 | 99.14 | 99.07 | 99.01 | 98.93 | |
| 763 | 99.30 | 99.23 | 99.15 | 99.08 | 99.01 | 98.94 | 98.88 | 98.80 | |
| 762 | 99.17 | 99.10 | 99.02 | 98.95 | 98.88 | 98.81 | 98.75 | 98.67 | |
| 761 | 99.04 | 98.97 | 98.89 | 98.82 | 98.75 | 98.68 | 98.62 | 98.54 | |
| 760 | 98.91 | 98.84 | 98.76 | 98.69 | 98.62 | 98.55 | 98.49 | 98.41 | |
| 759 | 98.78 | 98.71 | 98.63 | 98.57 | 98.49 | 98.42 | 98.36 | 98.28 | |
| 758 | 98.65 | 98.58 | 98.50 | 98.44 | 98.36 | 98.29 | 98.23 | 98.15 | |
| 757 | 98.52 | 98.45 | 98.37 | 98.30 | 98.23 | 98.16 | 98.10 | 98.02 | |
| 756 | 98.39 | 98.32 | 98.24 | 98.18 | 98.10 | 98.03 | 97.97 | 97.89 | |
| 755 | 98.26 | 98.19 | 98.11 | 98.05 | 97.97 | 97.90 | 97.84 | 97.76 | |
| 754 | 98.13 | 98.06 | 97.98 | 97.92 | 97.84 | 97.77 | 97.71 | 97.63 | |
| 753 | 98.00 | 97.93 | 97.85 | 97.79 | 97.71 | 97.64 | 97.58 | 97.50 | |
| 752 | 97.87 | 97.80 | 97.72 | 97.66 | 97.58 | 97.51 | 97.45 | 97.37 | |
| 751 | 97.74 | 97.67 | 97.59 | 97.53 | 97.45 | 97.38 | 97.32 | 97.24 | |
| 750 | 97.61 | 97.54 | 97.46 | 97.40 | 97.32 | 97.25 | 97.19 | 97.11 | |
| 749 | 97.48 | 97.41 | 97.33 | 97.27 | 97.20 | 97.12 | 97.05 | 96.98 | |
| 748 | 97.35 | 97.28 | 97.20 | 97.14 | 97.07 | 96.99 | 96.92 | 96.85 | |
| 747 | 97.22 | 97.15 | 97.07 | 97.01 | 96.94 | 96.86 | 96.79 | 96.72 | |
| 746 | 97.09 | 97.02 | 96.94 | 96.88 | 96.81 | 96.73 | 96.66 | 96.59 | |
| 745 | 96.96 | 96.89 | 96.81 | 96.75 | 96.68 | 96.61 | 96.54 | 96.47 | |
| | 4.6° | 4.8° | 5° | 5.2° | 5.4° | 5.6° | 5.8° | 6° | |
| 775 | 100.28 | 100.21 | 100.13 | 100.06 | 99.98 | 99.91 | 99.84 | 99.77 | |
| 774 | 100.15 | 100.08 | 100.00 | 99.93 | 99.85 | 99.78 | 99.71 | 99.65 | |
| 773 | 100.02 | 99.95 | 99.87 | 99.80 | 99.72 | 99.65 | 99.58 | 99.52 | |
| 772 | 99.89 | 99.82 | 99.75 | 99.68 | 99.60 | 99.53 | 99.46 | 99.39 | |
| 771 | 99.76 | 99.69 | 99.62 | 99.55 | 99.47 | 99.40 | 99.33 | 99.26 | |
| 770 | 99.63 | 99.56 | 99.49 | 99.42 | 99.34 | 99.27 | 99.20 | 99.13 | |
| 769 | 99.51 | 99.44 | 99.36 | 99.29 | 99.21 | 99.14 | 99.07 | 99.00 | |
| 768 | 99.38 | 99.31 | 99.23 | 99.16 | 99.08 | 99.01 | 98.94 | 98.87 | |
| 767 | 99.25 | 99.18 | 99.10 | 99.03 | 98.95 | 98.88 | 98.81 | 98.74 | |
| 766 | 99.12 | 99.05 | 98.97 | 98.90 | 98.82 | 98.75 | 98.68 | 98.62 | |
| 765 | 98.99 | 98.92 | 98.84 | 98.77 | 98.69 | 98.62 | 98.55 | 98.49 | |
| 764 | 98.86 | 98.79 | 98.71 | 98.64 | 98.56 | 98.49 | 98.42 | 98.36 | |
| 763 | 98.73 | 98.66 | 98.58 | 98.51 | 98.43 | 98.36 | 98.29 | 98.23 | |
| 762 | 98.60 | 98.53 | 98.45 | 98.38 | 98.30 | 98.23 | 98.16 | 98.10 | |
| 761 | 98.47 | 98.40 | 98.33 | 98.26 | 98.18 | 98.11 | 98.04 | 97.97 | |
| 760 | 98.34 | 98.27 | 98.20 | 98.13 | 98.05 | 97.98 | 97.91 | 97.84 | |
| 759 | 98.21 | 98.14 | 98.07 | 98.00 | 97.93 | 97.87 | 97.80 | 97.71 | |
| 758 | 98.08 | 98.01 | 97.94 | 97.87 | 97.80 | 97.74 | 97.67 | 97.58 | |
| 757 | 97.95 | 97.88 | 97.81 | 97.74 | 97.67 | 97.61 | 97.54 | 97.46 | |
| 756 | 97.82 | 97.75 | 97.68 | 97.61 | 97.54 | 97.48 | 97.41 | 97.33 | |
| 755 | 97.69 | 97.62 | 97.55 | 97.48 | 97.41 | 97.35 | 97.28 | 97.20 | |
| 754 | 97.56 | 97.49 | 97.42 | 97.35 | 97.28 | 97.22 | 97.15 | 97.07 | |
| 753 | 97.43 | 97.36 | 97.29 | 97.22 | 97.15 | 97.09 | 97.02 | 96.94 | |
| 752 | 97.30 | 97.23 | 97.16 | 97.09 | 97.02 | 96.96 | 96.89 | 96.81 | |
| 751 | 97.17 | 97.10 | 97.03 | 96.96 | 96.89 | 96.83 | 96.76 | 96.68 | |
| 750 | 97.04 | 96.97 | 96.90 | 96.83 | 96.76 | 96.70 | 96.63 | 96.56 | |
| 749 | 96.91 | 96.84 | 96.78 | 96.71 | 96.64 | 96.57 | 96.50 | 96.43 | |
| 748 | 96.78 | 96.71 | 96.65 | 96.58 | 96.51 | 96.44 | 96.37 | 96.30 | |
| 747 | 96.65 | 96.58 | 96.52 | 96.45 | 96.38 | 96.31 | 96.24 | 96.17 | |
| 746 | 96.52 | 96.45 | 96.39 | 96.32 | 96.25 | 96.18 | 96.11 | 96.04 | |
| 745 | 96.40 | 96.33 | 96.26 | 96.19 | 96.12 | 96.05 | 95.98 | 95.91 | |

ACID TABLES

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TABLE CII. (Continued)

| Barometric Pressure, Mm. of Mercury | Temperature, ° C. | | | | | | | | | |
|--|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 6.2° | 6.4° | 6.6° | 6.8° | 7° | 7.2° | 7.4° | 7.6° | 7.8° | 8° |
| 775..... | 99.70 | 99.63 | 99.56 | 99.49 | 99.42 | 99.35 | 99.28 | 99.21 | 99.14 | 99.06 |
| 774..... | 99.58 | 99.51 | 99.44 | 99.37 | 99.29 | 99.22 | 99.15 | 99.08 | 99.01 | 98.94 |
| 773..... | 99.45 | 99.38 | 99.31 | 99.24 | 99.16 | 99.09 | 99.02 | 98.95 | 98.88 | 98.81 |
| 772..... | 99.32 | 99.25 | 99.18 | 99.11 | 99.03 | 98.96 | 98.89 | 98.82 | 98.75 | 98.68 |
| 771..... | 99.19 | 99.12 | 99.05 | 98.98 | 98.91 | 98.84 | 98.77 | 98.70 | 98.63 | 98.56 |
| 770..... | 99.06 | 98.99 | 98.92 | 98.85 | 98.78 | 98.71 | 98.64 | 98.57 | 98.50 | 98.43 |
| 769..... | 98.93 | 98.86 | 98.79 | 98.72 | 98.65 | 98.58 | 98.51 | 98.45 | 98.38 | 98.30 |
| 768..... | 98.80 | 98.73 | 98.66 | 98.59 | 98.52 | 98.45 | 98.38 | 98.32 | 98.25 | 98.17 |
| 767..... | 98.67 | 98.60 | 98.53 | 98.46 | 98.39 | 98.32 | 98.25 | 98.19 | 98.12 | 98.04 |
| 766..... | 98.55 | 98.48 | 98.41 | 98.34 | 98.26 | 98.19 | 98.12 | 98.06 | 97.99 | 97.91 |
| 765..... | 98.42 | 98.35 | 98.28 | 98.21 | 98.14 | 98.07 | 98.00 | 97.94 | 97.87 | 97.79 |
| 764..... | 98.29 | 98.22 | 98.15 | 98.08 | 98.01 | 97.94 | 97.87 | 97.81 | 97.74 | 97.66 |
| 763..... | 98.16 | 98.09 | 98.02 | 97.95 | 97.88 | 97.81 | 97.74 | 97.68 | 97.61 | 97.53 |
| 762..... | 98.03 | 97.96 | 97.89 | 97.82 | 97.75 | 97.68 | 97.61 | 97.55 | 97.48 | 97.40 |
| 761..... | 97.90 | 97.83 | 97.76 | 97.69 | 97.62 | 97.55 | 97.48 | 97.42 | 97.35 | 97.27 |
| 760..... | 97.77 | 97.70 | 97.63 | 97.56 | 97.49 | 97.42 | 97.35 | 97.29 | 97.22 | 97.15 |
| 759..... | 97.64 | 97.57 | 97.50 | 97.43 | 97.37 | 97.30 | 97.23 | 97.17 | 97.10 | 97.02 |
| 758..... | 97.52 | 97.45 | 97.38 | 97.31 | 97.24 | 97.17 | 97.10 | 97.04 | 96.97 | 96.89 |
| 757..... | 97.39 | 97.32 | 97.25 | 97.18 | 97.11 | 97.04 | 96.97 | 96.91 | 96.84 | 96.76 |
| 756..... | 97.26 | 97.19 | 97.12 | 97.05 | 96.98 | 96.91 | 96.84 | 96.78 | 96.71 | 96.64 |
| 755..... | 97.13 | 97.06 | 96.99 | 96.92 | 96.85 | 96.78 | 96.71 | 96.65 | 96.58 | 96.51 |
| 754..... | 97.00 | 96.93 | 96.86 | 96.79 | 96.72 | 96.65 | 96.58 | 96.52 | 96.45 | 96.38 |
| 753..... | 96.87 | 96.80 | 96.73 | 96.66 | 96.60 | 96.53 | 96.46 | 96.40 | 96.33 | 96.25 |
| 752..... | 96.74 | 96.67 | 96.60 | 96.53 | 96.47 | 96.40 | 96.33 | 96.27 | 96.20 | 96.12 |
| 751..... | 96.61 | 96.54 | 96.47 | 96.40 | 96.34 | 96.27 | 96.20 | 96.14 | 96.07 | 96.00 |
| 750..... | 96.49 | 96.42 | 96.35 | 96.28 | 96.21 | 96.14 | 96.07 | 96.01 | 95.94 | 95.87 |
| 749..... | 96.36 | 96.30 | 96.23 | 96.16 | 96.08 | 96.01 | 95.94 | 95.88 | 95.81 | 95.74 |
| 748..... | 96.25 | 96.17 | 96.10 | 96.03 | 95.96 | 95.89 | 95.82 | 95.76 | 95.69 | 95.61 |
| 747..... | 96.12 | 96.04 | 95.97 | 95.90 | 95.83 | 95.76 | 95.69 | 95.63 | 95.56 | 95.49 |
| 746..... | 95.99 | 95.91 | 95.84 | 95.77 | 95.70 | 95.63 | 95.56 | 95.50 | 95.43 | 95.36 |
| 745..... | 95.86 | 95.78 | 95.71 | 95.64 | 95.57 | 95.50 | 95.43 | 95.37 | 95.30 | 95.23 |
| 744..... | 95.73 | 95.66 | 95.59 | 95.52 | 95.45 | 95.38 | 95.31 | 95.24 | 95.17 | 95.10 |
| 743..... | 95.60 | 95.53 | 95.46 | 95.39 | 95.32 | 95.25 | 95.18 | 95.11 | 95.04 | 94.97 |
| 742..... | 95.47 | 95.40 | 95.33 | 95.26 | 95.19 | 95.12 | 95.05 | 94.98 | 94.91 | 94.84 |
| 741..... | 95.34 | 95.27 | 95.20 | 95.13 | 95.06 | 94.99 | 94.92 | 94.85 | 94.78 | 94.71 |
| 740..... | 95.21 | 95.14 | 95.07 | 95.00 | 94.93 | 94.86 | 94.79 | 94.72 | 94.65 | 94.58 |
| 739..... | 95.08 | 95.01 | 94.94 | 94.87 | 94.80 | 94.73 | 94.66 | 94.59 | 94.52 | 94.45 |
| 738..... | 94.95 | 94.88 | 94.81 | 94.74 | 94.67 | 94.60 | 94.53 | 94.46 | 94.39 | 94.32 |
| 737..... | 94.82 | 94.75 | 94.68 | 94.61 | 94.54 | 94.47 | 94.40 | 94.33 | 94.26 | 94.19 |
| 736..... | 94.69 | 94.62 | 94.55 | 94.48 | 94.41 | 94.34 | 94.27 | 94.20 | 94.13 | 94.06 |
| 735..... | 94.56 | 94.49 | 94.42 | 94.35 | 94.28 | 94.21 | 94.14 | 94.07 | 94.00 | 93.93 |
| 734..... | 94.43 | 94.36 | 94.29 | 94.22 | 94.15 | 94.08 | 94.01 | 93.94 | 93.87 | 93.80 |
| 733..... | 94.30 | 94.23 | 94.16 | 94.09 | 94.02 | 93.95 | 93.88 | 93.81 | 93.74 | 93.67 |
| 732..... | 94.17 | 94.10 | 94.03 | 93.96 | 93.89 | 93.82 | 93.75 | 93.68 | 93.61 | 93.54 |
| 731..... | 94.04 | 93.97 | 93.90 | 93.83 | 93.76 | 93.69 | 93.62 | 93.55 | 93.48 | 93.41 |
| 730..... | 93.91 | 93.84 | 93.77 | 93.70 | 93.63 | 93.56 | 93.49 | 93.42 | 93.35 | 93.28 |
| 729..... | 93.78 | 93.71 | 93.64 | 93.57 | 93.50 | 93.43 | 93.36 | 93.29 | 93.22 | 93.15 |
| 728..... | 93.65 | 93.58 | 93.51 | 93.44 | 93.37 | 93.30 | 93.23 | 93.16 | 93.09 | 93.02 |
| 727..... | 93.52 | 93.45 | 93.38 | 93.31 | 93.24 | 93.17 | 93.10 | 93.03 | 92.96 | 92.89 |
| 726..... | 93.39 | 93.32 | 93.25 | 93.18 | 93.11 | 93.04 | 92.97 | 92.90 | 92.83 | 92.76 |
| 725..... | 93.26 | 93.19 | 93.12 | 93.05 | 92.98 | 92.91 | 92.84 | 92.77 | 92.70 | 92.63 |
| 724..... | 93.13 | 93.06 | 92.99 | 92.92 | 92.85 | 92.78 | 92.71 | 92.64 | 92.57 | 92.50 |
| 723..... | 93.00 | 92.93 | 92.86 | 92.79 | 92.72 | 92.65 | 92.58 | 92.51 | 92.44 | 92.37 |
| 722..... | 92.87 | 92.80 | 92.73 | 92.66 | 92.59 | 92.52 | 92.45 | 92.38 | 92.31 | 92.24 |
| 721..... | 92.74 | 92.67 | 92.60 | 92.53 | 92.46 | 92.39 | 92.32 | 92.25 | 92.18 | 92.11 |
| 720..... | 92.61 | 92.54 | 92.47 | 92.40 | 92.33 | 92.26 | 92.19 | 92.12 | 92.05 | 91.98 |
| 719..... | 92.48 | 92.41 | 92.34 | 92.27 | 92.20 | 92.13 | 92.06 | 91.99 | 91.92 | 91.85 |
| 718..... | 92.35 | 92.28 | 92.21 | 92.14 | 92.07 | 92.00 | 91.93 | 91.86 | 91.79 | 91.72 |
| 717..... | 92.22 | 92.15 | 92.08 | 92.01 | 91.94 | 91.87 | 91.80 | 91.73 | 91.66 | 91.59 |
| 716..... | 92.09 | 92.02 | 91.95 | 91.88 | 91.81 | 91.74 | 91.67 | 91.60 | 91.53 | 91.46 |
| 715..... | 91.96 | 91.89 | 91.82 | 91.75 | 91.68 | 91.61 | 91.54 | 91.47 | 91.40 | 91.33 |
| 714..... | 91.83 | 91.76 | 91.69 | 91.62 | 91.55 | 91.48 | 91.41 | 91.34 | 91.27 | 91.20 |
| 713..... | 91.70 | 91.63 | 91.56 | 91.49 | 91.42 | 91.35 | 91.28 | 91.21 | 91.14 | 91.07 |
| 712..... | 91.57 | 91.50 | 91.43 | 91.36 | 91.29 | 91.22 | 91.15 | 91.08 | 91.01 | 90.94 |
| 711..... | 91.44 | 91.37 | 91.30 | 91.23 | 91.16 | 91.09 | 91.02 | 90.95 | 90.88 | 90.81 |
| 710..... | 91.31 | 91.24 | 91.17 | 91.10 | 91.03 | 90.96 | 90.89 | 90.82 | 90.75 | 90.68 |
| 709..... | 91.18 | 91.11 | 91.04 | 90.97 | 90.90 | 90.83 | 90.76 | 90.69 | 90.62 | 90.55 |
| 708..... | 91.05 | 90.98 | 90.91 | 90.84 | 90.77 | 90.70 | 90.63 | 90.56 | 90.49 | 90.42 |
| 707..... | 90.92 | 90.85 | 90.78 | 90.71 | 90.64 | 90.57 | 90.50 | 90.43 | 90.36 | 90.29 |
| 706..... | 90.79 | 90.72 | 90.65 | 90.58 | 90.51 | 90.44 | 90.37 | 90.30 | 90.23 | 90.16 |
| 705..... | 90.66 | 90.59 | 90.52 | 90.45 | 90.38 | 90.31 | 90.24 | 90.17 | 90.10 | 90.03 |
| 704..... | 90.53 | 90.46 | 90.39 | 90.32 | 90.25 | 90.18 | 90.11 | 90.04 | 90.00 | 90.00 |
| 703..... | 90.40 | 90.33 | 90.26 | 90.19 | 90.12 | 90.05 | 90.00 | 90.00 | 90.00 | 90.00 |
| 702..... | 90.27 | 90.20 | 90.13 | 90.06 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 701..... | 90.14 | 90.07 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 700..... | 90.01 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 699..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 698..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 697..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 696..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 695..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 694..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 693..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 692..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 691..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 690..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 689..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 688..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 687..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 686..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 685..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 684..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 683..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 682..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 681..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 680..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 679..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 678..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 677..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 676..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 675..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 674..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 673..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 672..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 671..... | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| 670..... | 90.00 | 90.00 | 90.00 | 90.00 | | | | | | |

TABLE CII. (Continued)

| Barometric Pressure, Mm. of Mercury | Temperature, ° C. | | | | | | | | | |
|--|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 10.2° | 10.4° | 10.6° | 10.8° | 11° | 11.2° | 11.4° | 11.6° | 11.8° | 12° |
| 775..... | 98.30 | 98.23 | 98.16 | 98.09 | 98.02 | 97.96 | 97.80 | 97.82 | 97.75 | 97.68 |
| 774..... | 98.18 | 98.11 | 98.04 | 97.97 | 97.90 | 97.83 | 97.76 | 97.69 | 97.62 | 97.55 |
| 773..... | 98.05 | 97.98 | 97.91 | 97.84 | 97.77 | 97.70 | 97.63 | 97.56 | 97.49 | 97.42 |
| 772..... | 97.93 | 97.86 | 97.79 | 97.72 | 97.65 | 97.58 | 97.51 | 97.44 | 97.37 | 97.30 |
| 771..... | 97.80 | 97.73 | 97.66 | 97.59 | 97.52 | 97.45 | 97.38 | 97.31 | 97.24 | 97.17 |
| 770..... | 97.67 | 97.60 | 97.53 | 97.46 | 97.40 | 97.33 | 97.26 | 97.19 | 97.12 | 97.05 |
| 769..... | 97.54 | 97.47 | 97.40 | 97.33 | 97.26 | 97.20 | 97.13 | 97.06 | 96.99 | 96.92 |
| 768..... | 97.42 | 97.35 | 97.28 | 97.21 | 97.14 | 97.07 | 97.00 | 96.93 | 96.87 | 96.80 |
| 767..... | 97.29 | 97.22 | 97.15 | 97.08 | 97.01 | 96.95 | 96.88 | 96.81 | 96.74 | 96.67 |
| 766..... | 97.17 | 97.10 | 97.03 | 96.96 | 96.89 | 96.83 | 96.76 | 96.69 | 96.62 | 96.55 |
| 765..... | 97.04 | 96.97 | 96.90 | 96.83 | 96.76 | 96.70 | 96.63 | 96.56 | 96.49 | 96.42 |
| 764..... | 96.91 | 96.84 | 96.77 | 96.70 | 96.63 | 96.57 | 96.50 | 96.43 | 96.36 | 96.29 |
| 763..... | 96.78 | 96.71 | 96.64 | 96.57 | 96.50 | 96.44 | 96.37 | 96.30 | 96.23 | 96.16 |
| 762..... | 96.66 | 96.59 | 96.52 | 96.45 | 96.38 | 96.32 | 96.25 | 96.18 | 96.11 | 96.04 |
| 761..... | 96.52 | 96.46 | 96.39 | 96.32 | 96.25 | 96.19 | 96.12 | 96.05 | 95.98 | 95.91 |
| 760..... | 96.40 | 96.34 | 96.27 | 96.20 | 96.13 | 96.07 | 96.00 | 95.93 | 95.86 | 95.79 |
| 759..... | 96.28 | 96.21 | 96.14 | 96.07 | 96.00 | 95.94 | 95.87 | 95.80 | 95.73 | 95.66 |
| 758..... | 96.15 | 96.08 | 96.01 | 95.94 | 95.87 | 95.82 | 95.75 | 95.68 | 95.61 | 95.54 |
| 757..... | 96.02 | 95.95 | 95.88 | 95.81 | 95.74 | 95.68 | 95.62 | 95.55 | 95.48 | 95.41 |
| 756..... | 95.90 | 95.83 | 95.76 | 95.69 | 95.62 | 95.56 | 95.50 | 95.43 | 95.36 | 95.29 |
| 755..... | 95.77 | 95.70 | 95.63 | 95.56 | 95.49 | 95.43 | 95.37 | 95.30 | 95.23 | 95.16 |
| 754..... | 95.64 | 95.58 | 95.51 | 95.44 | 95.37 | 95.31 | 95.27 | 95.17 | 95.10 | 95.03 |
| 753..... | 95.52 | 95.45 | 95.38 | 95.31 | 95.24 | 95.18 | 95.11 | 95.04 | 94.97 | 94.90 |
| 752..... | 95.39 | 95.33 | 95.26 | 95.19 | 95.12 | 95.05 | 94.98 | 94.91 | 94.84 | 94.78 |
| 751..... | 95.27 | 95.20 | 95.13 | 95.06 | 94.99 | 94.92 | 94.85 | 94.78 | 94.72 | 94.65 |
| 750..... | 95.14 | 95.07 | 95.00 | 94.93 | 94.86 | 94.80 | 94.73 | 94.66 | 94.60 | 94.53 |
| 749..... | 95.01 | 94.94 | 94.87 | 94.80 | 94.73 | 94.67 | 94.61 | 94.54 | 94.47 | 94.40 |
| 748..... | 94.88 | 94.82 | 94.76 | 94.68 | 94.61 | 94.55 | 94.49 | 94.42 | 94.35 | 94.28 |
| 747..... | 94.76 | 94.69 | 94.62 | 94.55 | 94.48 | 94.42 | 94.36 | 94.29 | 94.22 | 94.15 |
| 746..... | 94.64 | 94.57 | 94.50 | 94.43 | 94.36 | 94.30 | 94.23 | 94.16 | 94.09 | 94.02 |
| 745..... | 94.51 | 94.44 | 94.37 | 94.30 | 94.23 | 94.17 | 94.10 | 94.03 | 93.96 | 93.89 |
| 744..... | 12.2° | 12.4° | 12.6° | 12.8° | 13° | 13.2° | 13.4° | 13.6° | 13.8° | 14° |
| 775..... | 97.61 | 97.53 | 97.46 | 97.40 | 97.33 | 97.26 | 97.19 | 97.12 | 97.06 | 96.99 |
| 774..... | 97.49 | 97.42 | 97.35 | 97.28 | 97.21 | 97.14 | 97.07 | 97.00 | 96.94 | 96.87 |
| 773..... | 97.36 | 97.29 | 97.22 | 97.15 | 97.08 | 97.02 | 96.95 | 96.88 | 96.82 | 96.75 |
| 772..... | 97.24 | 97.17 | 97.10 | 97.03 | 96.96 | 96.90 | 96.83 | 96.76 | 96.69 | 96.62 |
| 771..... | 97.11 | 97.04 | 96.97 | 96.90 | 96.83 | 96.77 | 96.71 | 96.64 | 96.57 | 96.50 |
| 770..... | 96.99 | 96.92 | 96.85 | 96.78 | 96.71 | 96.65 | 96.58 | 96.51 | 96.44 | 96.37 |
| 769..... | 96.85 | 96.78 | 96.72 | 96.65 | 96.58 | 96.52 | 96.46 | 96.39 | 96.32 | 96.25 |
| 768..... | 96.73 | 96.66 | 96.60 | 96.53 | 96.46 | 96.40 | 96.33 | 96.26 | 96.19 | 96.12 |
| 767..... | 96.61 | 96.54 | 96.47 | 96.40 | 96.33 | 96.27 | 96.21 | 96.14 | 96.07 | 96.00 |
| 766..... | 96.49 | 96.42 | 96.35 | 96.28 | 96.21 | 96.15 | 96.08 | 96.01 | 95.94 | 95.87 |
| 765..... | 96.36 | 96.29 | 96.22 | 96.15 | 96.08 | 96.02 | 95.96 | 95.89 | 95.82 | 95.75 |
| 764..... | 96.22 | 96.15 | 96.08 | 96.02 | 95.95 | 95.89 | 95.83 | 95.76 | 95.69 | 95.62 |
| 763..... | 96.09 | 96.02 | 95.95 | 95.88 | 95.82 | 95.76 | 95.70 | 95.63 | 95.56 | 95.50 |
| 762..... | 95.97 | 95.90 | 95.83 | 95.76 | 95.70 | 95.64 | 95.58 | 95.51 | 95.44 | 95.37 |
| 761..... | 95.84 | 95.77 | 95.71 | 95.64 | 95.57 | 95.51 | 95.45 | 95.39 | 95.32 | 95.25 |
| 760..... | 95.72 | 95.65 | 95.58 | 95.52 | 95.45 | 95.38 | 95.32 | 95.25 | 95.19 | 95.12 |
| 759..... | 95.60 | 95.53 | 95.46 | 95.39 | 95.32 | 95.26 | 95.20 | 95.13 | 95.06 | 95.00 |
| 758..... | 95.48 | 95.41 | 95.34 | 95.27 | 95.20 | 95.14 | 95.07 | 95.00 | 94.93 | 94.87 |
| 757..... | 95.35 | 95.28 | 95.21 | 95.14 | 95.07 | 95.01 | 94.94 | 94.87 | 94.81 | 94.75 |
| 756..... | 95.22 | 95.15 | 95.08 | 95.01 | 94.95 | 94.88 | 94.81 | 94.74 | 94.68 | 94.62 |
| 755..... | 95.09 | 95.02 | 94.95 | 94.88 | 94.82 | 94.75 | 94.68 | 94.62 | 94.56 | 94.50 |
| 754..... | 94.96 | 94.89 | 94.82 | 94.76 | 94.70 | 94.63 | 94.56 | 94.49 | 94.43 | 94.36 |
| 753..... | 94.83 | 94.76 | 94.69 | 94.63 | 94.57 | 94.50 | 94.43 | 94.37 | 94.31 | 94.24 |
| 752..... | 94.71 | 94.64 | 94.57 | 94.51 | 94.45 | 94.38 | 94.31 | 94.24 | 94.18 | 94.11 |
| 751..... | 94.58 | 94.51 | 94.44 | 94.38 | 94.32 | 94.25 | 94.19 | 94.12 | 94.06 | 93.99 |
| 750..... | 94.46 | 94.39 | 94.32 | 94.26 | 94.20 | 94.13 | 94.06 | 93.99 | 93.93 | 93.86 |
| 749..... | 94.33 | 94.26 | 94.19 | 94.13 | 94.07 | 94.00 | 93.93 | 93.86 | 93.80 | 93.74 |
| 748..... | 94.21 | 94.14 | 94.07 | 94.01 | 93.95 | 93.88 | 93.81 | 93.74 | 93.68 | 93.61 |
| 747..... | 94.08 | 94.01 | 93.94 | 93.88 | 93.82 | 93.75 | 93.68 | 93.62 | 93.56 | 93.49 |
| 746..... | 93.95 | 93.89 | 93.82 | 93.76 | 93.70 | 93.63 | 93.56 | 93.49 | 93.43 | 93.36 |

TABLE CII. (Continued)

| Barometric Pressure, Mm. of Mercury | Temperature, °C. | | | | | | | | | |
|--|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 14.2° | 14.4° | 14.6° | 14.8° | 15° | 15.2° | 15.4° | 15.6° | 15.8° | 16° |
| 775..... | 96.92 | 96.85 | 96.78 | 96.71 | 96.65 | 96.58 | 96.51 | 96.45 | 96.38 | 96.32 |
| 774..... | 96.80 | 96.73 | 96.66 | 96.59 | 96.53 | 96.47 | 96.40 | 96.33 | 96.26 | 96.20 |
| 773..... | 96.68 | 96.61 | 96.54 | 96.47 | 96.41 | 96.35 | 96.28 | 96.21 | 96.14 | 96.07 |
| 772..... | 96.55 | 96.48 | 96.41 | 96.34 | 96.28 | 96.22 | 96.16 | 96.09 | 96.02 | 95.95 |
| 771..... | 96.43 | 96.36 | 96.29 | 96.22 | 96.16 | 96.10 | 96.04 | 95.97 | 95.90 | 95.82 |
| 770..... | 96.30 | 96.23 | 96.16 | 96.09 | 96.03 | 95.98 | 95.92 | 95.85 | 95.78 | 95.72 |
| 769..... | 96.18 | 96.11 | 96.04 | 95.97 | 95.91 | 95.85 | 95.78 | 95.71 | 95.64 | 95.57 |
| 768..... | 96.05 | 95.98 | 95.91 | 95.84 | 95.78 | 95.72 | 95.65 | 95.59 | 95.52 | 95.45 |
| 767..... | 95.93 | 95.86 | 95.79 | 95.72 | 95.66 | 95.60 | 95.54 | 95.47 | 95.40 | 95.33 |
| 766..... | 95.80 | 95.73 | 95.66 | 95.59 | 95.53 | 95.47 | 95.41 | 95.34 | 95.27 | 95.20 |
| 765..... | 95.68 | 95.61 | 95.54 | 95.47 | 95.41 | 95.34 | 95.28 | 95.21 | 95.15 | 95.08 |
| 764..... | 95.55 | 95.48 | 95.41 | 95.34 | 95.28 | 95.22 | 95.15 | 95.08 | 95.02 | 94.95 |
| 763..... | 95.43 | 95.36 | 95.29 | 95.22 | 95.16 | 95.10 | 95.03 | 94.96 | 94.90 | 94.83 |
| 762..... | 95.30 | 95.23 | 95.16 | 95.09 | 95.03 | 94.97 | 94.91 | 94.84 | 94.77 | 94.70 |
| 761..... | 95.18 | 95.11 | 95.04 | 94.97 | 94.91 | 94.85 | 94.79 | 94.72 | 94.65 | 94.58 |
| 760..... | 95.05 | 94.98 | 94.91 | 94.84 | 94.78 | 94.72 | 94.66 | 94.60 | 94.53 | 94.46 |
| 759..... | 94.93 | 94.86 | 94.79 | 94.72 | 94.66 | 94.60 | 94.54 | 94.47 | 94.40 | 94.33 |
| 758..... | 94.80 | 94.73 | 94.66 | 94.59 | 94.53 | 94.47 | 94.42 | 94.35 | 94.28 | 94.21 |
| 757..... | 94.68 | 94.61 | 94.54 | 94.47 | 94.41 | 94.35 | 94.28 | 94.20 | 94.14 | 94.08 |
| 756..... | 94.55 | 94.48 | 94.41 | 94.35 | 94.29 | 94.23 | 94.16 | 94.09 | 94.03 | 93.96 |
| 755..... | 94.42 | 94.36 | 94.29 | 94.22 | 94.16 | 94.10 | 94.03 | 93.96 | 93.89 | 93.83 |
| 754..... | 94.30 | 94.23 | 94.16 | 94.10 | 94.04 | 93.97 | 93.90 | 93.84 | 93.77 | 93.70 |
| 753..... | 94.17 | 94.11 | 94.04 | 93.97 | 93.91 | 93.85 | 93.78 | 93.72 | 93.65 | 93.59 |
| 752..... | 94.04 | 93.98 | 93.91 | 93.85 | 93.79 | 93.73 | 93.66 | 93.60 | 93.53 | 93.46 |
| 751..... | 93.92 | 93.86 | 93.79 | 93.72 | 93.66 | 93.60 | 93.54 | 93.49 | 93.41 | 93.34 |
| 750..... | 93.79 | 93.73 | 93.66 | 93.60 | 93.54 | 93.48 | 93.42 | 93.36 | 93.29 | 93.21 |
| 749..... | 93.67 | 93.61 | 93.54 | 93.47 | 93.41 | 93.35 | 93.30 | 93.23 | 93.16 | 93.09 |
| 748..... | 93.55 | 93.48 | 93.41 | 93.35 | 93.29 | 93.23 | 93.16 | 93.09 | 93.03 | 92.96 |
| 747..... | 93.43 | 93.36 | 93.29 | 93.22 | 93.16 | 93.10 | 93.03 | 92.97 | 92.91 | 92.84 |
| 746..... | 93.30 | 93.23 | 93.16 | 93.10 | 93.04 | 92.98 | 92.91 | 92.85 | 92.79 | 92.72 |
| 745..... | 93.18 | 93.11 | 93.04 | 92.97 | 92.91 | 92.86 | 92.79 | 92.73 | 92.66 | 92.59 |
| 744..... | 16.2° | 16.4° | 16.6° | 16.8° | 17° | 17.2° | 17.4° | 17.6° | 17.8° | 18° |
| 743..... | 94.25 | 94.18 | 94.11 | 94.04 | 93.97 | 93.90 | 93.84 | 93.77 | 93.70 | 93.63 |
| 742..... | 94.13 | 94.06 | 93.99 | 93.92 | 93.85 | 93.78 | 93.72 | 93.65 | 93.58 | 93.51 |
| 741..... | 94.00 | 93.93 | 93.86 | 93.79 | 93.72 | 93.65 | 93.58 | 93.51 | 93.44 | 93.37 |
| 740..... | 93.88 | 93.81 | 93.74 | 93.67 | 93.60 | 93.53 | 93.46 | 93.39 | 93.32 | 93.25 |
| 739..... | 93.76 | 93.69 | 93.62 | 93.55 | 93.48 | 93.41 | 93.34 | 93.27 | 93.20 | 93.13 |
| 738..... | 93.64 | 93.57 | 93.50 | 93.43 | 93.36 | 93.29 | 93.22 | 93.15 | 93.08 | 93.01 |
| 737..... | 93.51 | 93.44 | 93.37 | 93.30 | 93.23 | 93.16 | 93.09 | 93.02 | 92.95 | 92.88 |
| 736..... | 93.39 | 93.32 | 93.25 | 93.18 | 93.11 | 93.04 | 92.97 | 92.90 | 92.83 | 92.76 |
| 735..... | 93.27 | 93.20 | 93.13 | 93.06 | 92.99 | 92.92 | 92.85 | 92.78 | 92.71 | 92.64 |
| 734..... | 93.15 | 93.08 | 93.01 | 92.94 | 92.87 | 92.80 | 92.73 | 92.66 | 92.59 | 92.52 |
| 733..... | 93.03 | 92.96 | 92.89 | 92.82 | 92.75 | 92.68 | 92.61 | 92.54 | 92.47 | 92.40 |
| 732..... | 92.91 | 92.84 | 92.77 | 92.70 | 92.63 | 92.56 | 92.49 | 92.42 | 92.35 | 92.28 |
| 731..... | 92.79 | 92.72 | 92.65 | 92.58 | 92.51 | 92.44 | 92.37 | 92.30 | 92.23 | 92.16 |
| 730..... | 92.67 | 92.60 | 92.53 | 92.46 | 92.39 | 92.32 | 92.25 | 92.18 | 92.11 | 92.04 |
| 729..... | 92.55 | 92.48 | 92.41 | 92.34 | 92.27 | 92.20 | 92.13 | 92.06 | 91.99 | 91.92 |
| 728..... | 92.43 | 92.36 | 92.29 | 92.22 | 92.15 | 92.08 | 92.01 | 91.94 | 91.87 | 91.80 |
| 727..... | 92.31 | 92.24 | 92.17 | 92.10 | 92.03 | 91.96 | 91.89 | 91.82 | 91.75 | 91.68 |
| 726..... | 92.19 | 92.12 | 92.05 | 91.98 | 91.91 | 91.84 | 91.77 | 91.70 | 91.63 | 91.56 |
| 725..... | 92.07 | 92.00 | 91.93 | 91.86 | 91.79 | 91.72 | 91.65 | 91.58 | 91.51 | 91.44 |
| 724..... | 91.95 | 91.88 | 91.81 | 91.74 | 91.67 | 91.60 | 91.53 | 91.46 | 91.39 | 91.32 |
| 723..... | 91.83 | 91.76 | 91.69 | 91.62 | 91.55 | 91.48 | 91.41 | 91.34 | 91.27 | 91.20 |
| 722..... | 91.71 | 91.64 | 91.57 | 91.50 | 91.43 | 91.36 | 91.29 | 91.22 | 91.15 | 91.08 |
| 721..... | 91.59 | 91.52 | 91.45 | 91.38 | 91.31 | 91.24 | 91.17 | 91.10 | 91.03 | 90.96 |
| 720..... | 91.47 | 91.40 | 91.33 | 91.26 | 91.19 | 91.12 | 91.05 | 90.98 | 90.91 | 90.84 |
| 719..... | 91.35 | 91.28 | 91.21 | 91.14 | 91.07 | 91.00 | 90.93 | 90.86 | 90.79 | 90.72 |
| 718..... | 91.23 | 91.16 | 91.09 | 91.02 | 90.95 | 90.88 | 90.81 | 90.74 | 90.67 | 90.60 |
| 717..... | 91.11 | 91.04 | 90.97 | 90.90 | 90.83 | 90.76 | 90.69 | 90.62 | 90.55 | 90.48 |
| 716..... | 90.99 | 90.92 | 90.85 | 90.78 | 90.71 | 90.64 | 90.57 | 90.50 | 90.43 | 90.36 |
| 715..... | 90.87 | 90.80 | 90.73 | 90.66 | 90.59 | 90.52 | 90.45 | 90.38 | 90.31 | 90.24 |
| 714..... | 90.75 | 90.68 | 90.61 | 90.54 | 90.47 | 90.40 | 90.33 | 90.26 | 90.19 | 90.12 |
| 713..... | 90.63 | 90.56 | 90.49 | 90.42 | 90.35 | 90.28 | 90.21 | 90.14 | 90.07 | 90.00 |
| 712..... | 90.51 | 90.44 | 90.37 | 90.30 | 90.23 | 90.16 | 90.09 | 90.02 | 89.95 | 89.88 |
| 711..... | 90.39 | 90.32 | 90.25 | 90.18 | 90.11 | 90.04 | 89.97 | 89.90 | 89.83 | 89.76 |
| 710..... | 90.27 | 90.20 | 90.13 | 90.06 | 89.99 | 89.92 | 89.85 | 89.78 | 89.71 | 89.64 |
| 709..... | 90.15 | 90.08 | 90.01 | 89.94 | 89.87 | 89.80 | 89.73 | 89.66 | 89.59 | 89.52 |
| 708..... | 90.03 | 89.96 | 89.89 | 89.82 | 89.75 | 89.68 | 89.61 | 89.54 | 89.47 | 89.40 |
| 707..... | 89.91 | 89.84 | 89.77 | 89.70 | 89.63 | 89.56 | 89.49 | 89.42 | 89.35 | 89.28 |
| 706..... | 89.79 | 89.72 | 89.65 | 89.58 | 89.51 | 89.44 | 89.37 | 89.30 | 89.23 | 89.16 |
| 705..... | 89.67 | 89.60 | 89.53 | 89.46 | 89.39 | 89.32 | 89.25 | 89.18 | 89.11 | 89.04 |
| 704..... | 89.55 | 89.48 | 89.41 | 89.34 | 89.27 | 89.20 | 89.13 | 89.06 | 88.99 | 88.92 |
| 703..... | 89.43 | 89.36 | 89.29 | 89.22 | 89.15 | 89.08 | 89.01 | 88.94 | 88.87 | 88.80 |
| 702..... | 89.31 | 89.24 | 89.17 | 89.10 | 89.03 | 88.96 | 88.89 | 88.82 | 88.75 | 88.68 |
| 701..... | 89.19 | 89.12 | 89.05 | 88.98 | 88.91 | 88.84 | 88.77 | 88.70 | 88.63 | 88.56 |
| 700..... | 89.07 | 89.00 | 88.93 | 88.86 | 88.79 | 88.72 | 88.65 | 88.58 | 88.51 | 88.44 |
| 699..... | 88.95 | 88.88 | 88.81 | 88.74 | 88.67 | 88.60 | 88.53 | 88.46 | 88.39 | 88.32 |
| 698..... | 88.83 | 88.76 | 88.69 | 88.62 | 88.55 | 88.48 | 88.41 | 88.34 | 88.27 | 88.20 |
| 697..... | 88.71 | 88.64 | 88.57 | 88.50 | 88.43 | 88.36 | 88.29 | 88.22 | 88.15 | 88.08 |
| 696..... | 88.59 | 88.52 | 88.45 | 88.38 | 88.31 | 88.24 | 88.17 | 88.10 | 88.03 | 87.96 |
| 695..... | 88.47 | 88.40 | 88.33 | 88.26 | 88.19 | 88.12 | 88.05 | 87.98 | 87.91 | 87.84 |
| 694..... | 88.35 | 88.28 | 88.21 | 88.14 | 88.07 | 88.00 | 87.93 | 87.86 | 87.79 | 87.72 |
| 693..... | 88.23 | 88.16 | 88.09 | 88.02 | 87.95 | 87.88 | 87.81 | 87.74 | 87.67 | 87.60 |
| 692..... | 88.11 | 88.04 | 87.97 | 87.90 | 87.83 | 87.76 | 87.69 | 87.62 | 87.55 | 87.48 |
| 691..... | 87.99 | 87.92 | 87.85 | 87.78 | 87.71 | 87.64 | 87.57 | 87.50 | 87.43 | 87.36 |
| 690..... | 87.87 | 87.80 | 87.73 | 87.66 | 87.59 | 87.52 | 87.45 | 87.38 | 87.31 | 87.24 |
| 689..... | 87.75 | 87.68 | 87.61 | 87.54 | 87.47 | 87.40 | 87.33 | 87.26 | 87.19 | 87.12 |
| 688..... | 87.63 | 87.56 | 87.49 | 87.42 | 87.35 | 87.28 | 87.21 | 87.14 | 87.07 | 87.00 |
| 687..... | 87.51 | 87.44 | 87.37 | 87.30 | 87.23 | 87.16 | 87.09 | 87.02 | 86.95 | 86.88 |
| 686..... | 87.39 | 87.32 | 87.25 | 87.18 | 87.11 | 87.04 | 86.97 | 86.90 | 86.83 | 86.76 |
| 685..... | 87.27 | 87.20 | 87.13 | 87.06 | 86.99 | 86.92 | 86.85 | 86.78 | 86.71 | 86.64 |
| 684..... | 87.15 | 87.08 | 87.01 | 86.94 | 86.87 | 86.80 | 86.73 | 86.66 | 86.59 | 86.52 |
| 683..... | 87.03 | 86.96 | 86.89 | 86.82 | 86.75 | 86.68 | 86.61 | 86.54 | 86.47 | 86.40 |
| 682..... | 86.91 | 86.84 | 86.77 | 86.70 | 86.63 | 86.56 | 86.49 | 86.42 | 86.35 | 86.28 |
| 681..... | 86.79 | 86.72 | 86.65 | 86.58 | 86.51 | 86.44 | 86.37 | 86.30 | 86.23 | 86.16 |
| 680..... | 86.67 | 86.60 | 86.53 | 86.46 | 86.39 | 86.32 | 86.25 | 86.18 | 86.11 | 86.04 |
| 679..... | 86.55 | 86.48 | 86.41 | 86.34 | 86.27 | 86.20 | 86.13 | 86.06 | 85.99 | 85.92 |
| 678..... | 86.43 | 86.36 | 86.29 | 86.22 | 86.15 | 86.08 | 86.01 | 85.94 | 85.87 | 85.80 |
| 677..... | 86.31 | 86.24 | 86.17 | 86.10 | 86.03 | 85.96 | 85.89 | 85.82 | 85.75 | 85.68 |
| 676..... | 86.19 | 86.12 | 86.05 | 85.98 | 85.91 | 85.84 | 85.77 | 85.70 | 85.63 | 85.56 |
| 675..... | 86.07 | 86.00 | 85.93 | 85.86 | 85.79 | 85.72 | 85.65 | 85.58 | 85.51 | 85.44 |
| 674..... | 85.95 | 85.88 | 85.81 | 85.74 | 85.67 | 85.60 | 85.53 | 85.46 | 85.39 | 85.32 |
| 673..... | 85.83 | 85.76 | 85.69 | 85.62 | 85.55 | 85.48 | 85.41 | 85.34 | 85.27 | 85.20 |
| 672..... | 85.71 | 85.64 | 85.57 | 85.50 | 85.43 | 85.36 | 85.29 | 85.22 | 85.15 | 85.08 |
| 671..... | 85.59 | 85.52 | 85.45 | 85.38 | 85.31 | 85.24 | 85.17 | 85.10 | 85.03 | 84.96 |
| 670..... | 85.47 | 85.40 | 85.33 | 85.26 | 8 | | | | | |

TABLE CII. (Continued)

| Barometric Pressure, mm. of Mercury | Temperature, ° C. | | | | | | | | | |
|--|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 18.2° | 18.4° | 18.6° | 18.8° | 19.0° | 19.2° | 19.4° | 19.6° | 19.8° | 20° |
| 776..... | 95.59 | 95.53 | 95.46 | 95.40 | 95.33 | 95.27 | 95.20 | 95.14 | 95.08 | 95.01 |
| 774..... | 95.47 | 95.41 | 95.34 | 95.28 | 95.21 | 95.14 | 95.08 | 95.02 | 94.95 | 94.88 |
| 773..... | 95.35 | 95.29 | 95.22 | 95.16 | 95.09 | 95.02 | 94.96 | 94.90 | 94.83 | 94.76 |
| 772..... | 95.23 | 95.17 | 95.10 | 95.04 | 94.97 | 94.91 | 94.85 | 94.78 | 94.71 | 94.64 |
| 771..... | 95.10 | 95.05 | 94.98 | 94.91 | 94.86 | 94.80 | 94.73 | 94.66 | 94.59 | 94.52 |
| 770..... | 94.98 | 94.91 | 94.85 | 94.78 | 94.71 | 94.65 | 94.58 | 94.52 | 94.46 | 94.39 |
| 769..... | 94.86 | 94.79 | 94.73 | 94.66 | 94.59 | 94.53 | 94.46 | 94.40 | 94.34 | 94.27 |
| 768..... | 94.73 | 94.66 | 94.60 | 94.54 | 94.47 | 94.41 | 94.34 | 94.28 | 94.22 | 94.15 |
| 767..... | 94.61 | 94.54 | 94.48 | 94.42 | 94.36 | 94.29 | 94.21 | 94.15 | 94.09 | 94.02 |
| 766..... | 94.49 | 94.42 | 94.36 | 94.30 | 94.23 | 94.17 | 94.09 | 94.03 | 93.97 | 93.90 |
| 765..... | 94.37 | 94.30 | 94.24 | 94.18 | 94.11 | 94.04 | 93.97 | 93.91 | 93.85 | 93.78 |
| 764..... | 94.24 | 94.18 | 94.12 | 94.06 | 93.99 | 93.92 | 93.85 | 93.79 | 93.73 | 93.66 |
| 763..... | 94.12 | 94.06 | 94.00 | 93.94 | 93.87 | 93.80 | 93.73 | 93.67 | 93.60 | 93.53 |
| 762..... | 94.00 | 93.94 | 93.88 | 93.82 | 93.75 | 93.68 | 93.61 | 93.55 | 93.48 | 93.41 |
| 761..... | 93.88 | 93.82 | 93.76 | 93.69 | 93.62 | 93.55 | 93.48 | 93.41 | 93.35 | 93.28 |
| 760..... | 93.74 | 93.67 | 93.61 | 93.55 | 93.49 | 93.42 | 93.36 | 93.29 | 93.23 | 93.17 |
| 759..... | 93.62 | 93.55 | 93.49 | 93.43 | 93.36 | 93.30 | 93.24 | 93.17 | 93.11 | 93.04 |
| 758..... | 93.50 | 93.43 | 93.37 | 93.31 | 93.24 | 93.18 | 93.12 | 93.05 | 92.99 | 92.92 |
| 757..... | 93.38 | 93.31 | 93.25 | 93.19 | 93.12 | 93.06 | 93.00 | 92.93 | 92.87 | 92.80 |
| 756..... | 93.25 | 93.19 | 93.12 | 93.06 | 93.00 | 92.94 | 92.88 | 92.81 | 92.75 | 92.68 |
| 755..... | 93.13 | 93.07 | 93.00 | 92.94 | 92.88 | 92.82 | 92.76 | 92.69 | 92.63 | 92.56 |
| 754..... | 93.00 | 92.94 | 92.88 | 92.82 | 92.76 | 92.70 | 92.64 | 92.57 | 92.50 | 92.43 |
| 753..... | 92.88 | 92.82 | 92.76 | 92.70 | 92.64 | 92.58 | 92.52 | 92.45 | 92.38 | 92.31 |
| 752..... | 92.76 | 92.70 | 92.64 | 92.58 | 92.52 | 92.46 | 92.39 | 92.32 | 92.26 | 92.19 |
| 751..... | 92.64 | 92.58 | 92.52 | 92.46 | 92.40 | 92.33 | 92.26 | 92.19 | 92.12 | 92.06 |
| 750..... | 92.51 | 92.46 | 92.40 | 92.35 | 92.28 | 92.19 | 92.12 | 92.06 | 92.00 | 91.94 |
| 749..... | 92.38 | 92.32 | 92.26 | 92.20 | 92.13 | 92.07 | 92.01 | 91.94 | 91.88 | 91.82 |
| 748..... | 92.26 | 92.20 | 92.14 | 92.08 | 92.01 | 91.95 | 91.88 | 91.82 | 91.76 | 91.70 |
| 747..... | 92.14 | 92.08 | 92.02 | 91.95 | 91.89 | 91.83 | 91.76 | 91.70 | 91.64 | 91.57 |
| 746..... | 92.02 | 91.96 | 91.90 | 91.83 | 91.77 | 91.71 | 91.64 | 91.59 | 91.52 | 91.45 |
| 745..... | 91.90 | 91.84 | 91.78 | 91.71 | 91.65 | 91.59 | 91.53 | 91.47 | 91.40 | 91.33 |
| 744..... | 20.3° | 20.4° | 20.6° | 20.8° | 21° | 21.2° | 21.4° | 21.6° | 21.8° | 22° |
| 743..... | 94.95 | 94.88 | 94.81 | 94.75 | 94.68 | 94.61 | 94.54 | 94.48 | 94.42 | 94.36 |
| 742..... | 94.81 | 94.74 | 94.68 | 94.62 | 94.56 | 94.49 | 94.42 | 94.36 | 94.30 | 94.24 |
| 741..... | 94.69 | 94.62 | 94.56 | 94.50 | 94.44 | 94.37 | 94.30 | 94.24 | 94.18 | 94.12 |
| 740..... | 94.57 | 94.50 | 94.44 | 94.38 | 94.31 | 94.24 | 94.17 | 94.11 | 94.05 | 93.99 |
| 739..... | 94.45 | 94.38 | 94.32 | 94.26 | 94.19 | 94.12 | 94.05 | 93.99 | 93.93 | 93.87 |
| 738..... | 94.33 | 94.26 | 94.20 | 94.14 | 94.07 | 94.00 | 93.93 | 93.87 | 93.81 | 93.75 |
| 737..... | 94.20 | 94.14 | 94.08 | 94.01 | 93.95 | 93.88 | 93.81 | 93.75 | 93.69 | 93.63 |
| 736..... | 94.08 | 94.02 | 93.96 | 93.89 | 93.83 | 93.76 | 93.69 | 93.63 | 93.57 | 93.51 |
| 735..... | 93.96 | 93.90 | 93.83 | 93.77 | 93.70 | 93.63 | 93.57 | 93.51 | 93.45 | 93.39 |
| 734..... | 93.84 | 93.78 | 93.71 | 93.64 | 93.58 | 93.51 | 93.44 | 93.38 | 93.32 | 93.26 |
| 733..... | 93.72 | 93.66 | 93.59 | 93.52 | 93.46 | 93.39 | 93.32 | 93.26 | 93.20 | 93.14 |
| 732..... | 93.60 | 93.54 | 93.47 | 93.40 | 93.34 | 93.27 | 93.20 | 93.14 | 93.08 | 93.02 |
| 731..... | 93.48 | 93.42 | 93.35 | 93.28 | 93.22 | 93.15 | 93.08 | 93.02 | 92.96 | 92.90 |
| 730..... | 93.35 | 93.29 | 93.23 | 93.16 | 93.10 | 93.03 | 92.96 | 92.90 | 92.84 | 92.78 |
| 729..... | 93.23 | 93.17 | 93.10 | 93.03 | 92.96 | 92.91 | 92.84 | 92.77 | 92.71 | 92.65 |
| 728..... | 93.11 | 93.05 | 92.98 | 92.91 | 92.86 | 92.79 | 92.73 | 92.65 | 92.59 | 92.53 |
| 727..... | 92.99 | 92.93 | 92.86 | 92.79 | 92.74 | 92.67 | 92.60 | 92.53 | 92.47 | 92.41 |
| 726..... | 92.87 | 92.81 | 92.74 | 92.67 | 92.62 | 92.55 | 92.48 | 92.41 | 92.35 | 92.29 |
| 725..... | 92.74 | 92.68 | 92.62 | 92.55 | 92.49 | 92.42 | 92.35 | 92.29 | 92.23 | 92.17 |
| 724..... | 92.61 | 92.55 | 92.49 | 92.42 | 92.37 | 92.30 | 92.23 | 92.17 | 92.11 | 92.05 |
| 723..... | 92.49 | 92.43 | 92.36 | 92.30 | 92.25 | 92.18 | 92.11 | 92.05 | 91.99 | 91.93 |
| 722..... | 92.36 | 92.30 | 92.24 | 92.18 | 92.13 | 92.06 | 91.99 | 91.92 | 91.85 | 91.79 |
| 721..... | 92.24 | 92.18 | 92.12 | 92.06 | 92.01 | 91.94 | 91.87 | 91.80 | 91.74 | 91.68 |
| 720..... | 92.12 | 92.06 | 92.00 | 91.93 | 91.88 | 91.81 | 91.74 | 91.68 | 91.62 | 91.56 |
| 719..... | 92.00 | 91.93 | 91.88 | 91.81 | 91.75 | 91.68 | 91.62 | 91.56 | 91.50 | 91.44 |
| 718..... | 91.88 | 91.82 | 91.76 | 91.69 | 91.63 | 91.56 | 91.50 | 91.44 | 91.38 | 91.32 |
| 717..... | 91.76 | 91.70 | 91.64 | 91.57 | 91.50 | 91.43 | 91.37 | 91.31 | 91.25 | 91.19 |
| 716..... | 91.64 | 91.58 | 91.52 | 91.45 | 91.38 | 91.31 | 91.25 | 91.19 | 91.13 | 91.07 |
| 715..... | 91.51 | 91.45 | 91.39 | 91.32 | 91.26 | 91.19 | 91.13 | 91.07 | 91.01 | 90.95 |
| 714..... | 91.39 | 91.33 | 91.27 | 91.20 | 91.14 | 91.07 | 91.01 | 90.95 | 90.89 | 90.83 |
| 713..... | 91.27 | 91.21 | 91.15 | 91.08 | 91.02 | 90.95 | 90.89 | 90.83 | 90.77 | 90.71 |

